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Mixed-Ligand 1,2-Diimine Ethylene-1,2-dithiolate Complexes of Nickel, Palladium, and Platinum

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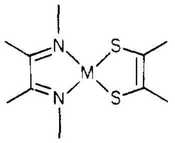
The discussion of mixed-valence (MV) or intervalence (IT) transition-metal complexes has been largely restricted to systems containing a reducing and an oxidizing metal center.[2–4] If the metal–metal interaction is weak, definite oxidation states can be assigned to the metals and charge-transfer (CT) or IT electronic transitions from the reduced to the oxidized metal occur at relatively low energies. Mononuclear metal complexes in which a ligand occurs in different oxidation states ($L_{red}ML_{ox}$) are also MV compounds.[5,6] However, in the electronic spectra of complexes containing catecholate and *o*-semiquinone as MV ligands, IT absorptions were not detected.[6] MV ligands seem also to be present in the 1,2-dithiolene complexes of Ni(II), Pd(II), and Pt(II)[7] (A).

A

The electronic structure is described by two equivalent resonance forms.[8] The highest occupied ($2b_{1u}$) and the lowest unoccupied ($3b_{2g}$) ligand orbitals are equally delocalized over both ligands.[8–10] The $2b_{1u} \to 3b_{2g}$ electronic transition has then no CT contribution. However, one of both resonance forms may prevail in the ground state if the complex becomes unsymmetric by the proper choice of substituents at the ligands.[11] The ground state is represented almost exclusively by one of both mesomeric forms, when the 1,2-dithioketone is replaced by 1,2-diimine as oxidizing ligand[12] (B).



B

The $2b_{1u} \to 3b_{2g}$ (in D_{2h} symmetry) transition becomes now a CT or IT transition from the reducing 1,2-ethylenedithiolate to the oxidizing 1,2-diimine ligand.[12,13] The present investigation was undertaken to gain more insight into the electronic structure of these ligand-based MV complexes with particular reference to the influence of the metal.

Table I. Electrochemical Data for (1,2-Diimine)(ethylene-1,2-dithiolate)metal(II) Complexes[a]

	redn		oxidn	
complex	$E_0'(1)$[b]	$E_{p/2}(2)$[c]	$E_{p/2}(1)$	$E_{p/2}(2)$[g]
Ni(BABA)(MNT)	−0.70	−1.50	+0.8[d]	
Pd(BABA)(MNT)	−0.78	−1.50	+1.18[e]	
Pt(BAB)(MNT)	−0.78	−1.42	+1.20[f]	
Ni(BABA)(TT)	−1.00	−1.66	+0.48[d]	
Pd(BABA)(TT)	−0.98	−1.66	+0.58[d]	+1.20
Pt(BABA)(TT)	−0.94	−1.66	+0.64[b]	+1.20, +1.34

[a] Cyclic voltammograms at a Pt-disk electrode in 0.1 M *n*-$BuNClO_4/CH_3CN$; potentials in V vs. SCE. [b] Pure Nernstian waves for $v = 0.5–20\ V\ s^{-1}$. [c] Quasi-reversible waves; potentials given for $v = 0.2\ V\ s^{-1}$. [d] Chemically irreversible waves with peak heights corresponding to two-electron oxidations. [e] Beginning reversibility at $v > 20\ V\ s^{-1}$. [f] Nernstian behavior at $v \geqslant 2\ V\ s^{-1}$; E_0 given. [g] Irreversible waves; potentials given for $v = 0.2\ V\ s^{-1}$.

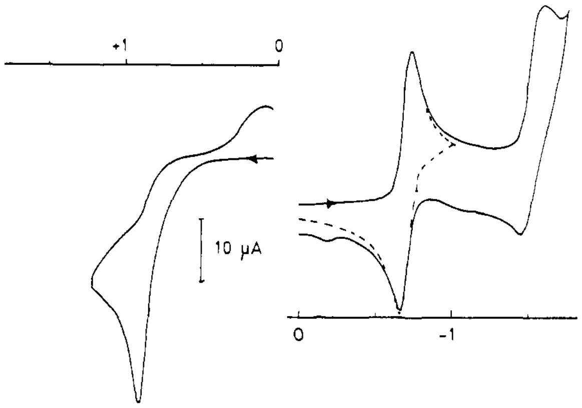


Figure 1. Cyclic voltammetric oxidation and reduction of Ni(BABA)(MNT) (1 mM in 0.1 M $TBAP/CH_3CN$) at a 2-mm o.d. Pt disk (scan rate 0.2 V s^{-1}; potentials vs. SCE).

Results and Discussion

Synthesis. Six complexes of the type M(1,2-diimine)(ethylene-1,2-dithiolate) (III) were prepared with nickel, palladium, and platinum as central metal, biacetyl bis(anil) (BABA) as diimine, and disulfidomaleonitrile (MNT^{2-}) and 3,4-toluenedithiolate (TT^{2-}) as dithiolate ligands. The complex Ni(BABA)(MNT) was synthesized according to a procedure by Miller and Dance.[12] The compound Ni(BABA)(TT) was obtained by a similar method (eq 1). For the palladium

$$Ni(BABA)_2Cl_2 + H_2TT \to Ni(BABA)(TT) + BABA + 2HCl \tag{1}$$

complexes $Pd(benzonitrile)_2Cl_2$ was used as starting material. It reacted with BABA to yield $Pd(BABA)Cl_2$. It was not necessary to isolate this compound. Upon addition of Na_2MNT or H_2TT the desired complexes were obtained (eq 2). A different route was employed for the synthesis of the

$$Pd(BABA)Cl_2 + Na_2MNT \to Pd(BABA)(MNT) + 2NaCl \tag{2a}$$

$$Pd(BABA)Cl_2 + H_2TT \to Pd(BABA)(TT) + 2HCl \tag{2b}$$

platinum complexes. In solution it was apparently not possible to achieve a coordination of BABA to platinum. However, finely ground Na_2PtCl_4 reacted in a melt of BABA at 170 °C. The stoichiometry of the Pt(BABA) complex formed in this reaction was not established. In analogy to other diimine (bipyridyl and *o*-phenanthroline) complexes of platinum, $Pt(BABA)Cl_2$ was most likely formed. An isolation of this compound was not required. The crude product reacted with Na_2MNT or H_2TT (see eq 2) to yield Pt(BABA)(MNT) and Pt(BABA)(TT). All six complexes crystallize as dark blue to deep purple solids.

Electrochemistry. Cyclic voltammetric data are presented in Table I and Figure 1. All six complexes undergo a

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Table II. Electronic Absorption Spectral Data for (1,2-Diimine)(ethylene-1,2-dithiolate)metal(II) Complexes^a

	band maxima^b									
	acetonitrile		acetone		methylene chloride		chloroform		carbon tetrachloride	
complex	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_1$	$\bar{\nu}_2$
Ni(BABA)(TT)	15 700 (7200)	16 530 sh (6840)	14 920	16 340 sh	14 370	15 770 sh	13 890	15 380 sh	12 990	14 530 sh
Pd(BABA)(TT)	16 050 (5000)	19 600 (2400)	15 430		14 530		13 490	14 450 sh	11 960	13 550
Pt(BABA)(TT)	15 800 (14 800)		15 150	16 200	14 660	15 670 sh	14 200	15 240 sh	13 490	14 580
Ni(BABA)(MNT)	17 540 sh (4600)	18 380 (5130)	17 240 sh	18 250	16 020 sh	17 180	15 530 sh	16 660	15 130	16 290
Pd(BABA)(MNT)	18 050 sh (1960)	19 760 (2270)	17 800 sh	19 530	16 670	18 650 sh	16 000	17 920 sh	15 700	17 120 sh
Pt(BABA)(MNT)	17 760 (7590)		17 420	17 920 sh	16 130	17 180 sh	15 630	16 670 sh	15 100	16 230 sh

^{a} Only absorption bands in the visible region. ^{b} Frequencies in cm^{-1}; extinction coefficients (L mol^{-1} cm^{-1}) in parentheses; sh = shoulder.

chemically and kinetically reversible one-electron reduction, near −0.8 V for the MNT series and near −1.0 V for the TT types. Second-reduction waves are also observed, which are chemically reversible but non-Nernstian. Again, the potentials are slightly more negative in the TT series.

In the oxidation of the complexes, reversible one-electron waves are found only for the Pt complexes (detailed information in Figure 1 and the footnotes of Table I). Increasing chemical irreversibility is observed on going from Pt to Ni, ultimately giving rise to overall two-electron oxidation waves. This phenomenon is usually associated with coupled electron transfer and chemical steps (e.g. ECE mechanism). In this view, the remarkably facile oxidation of the Ni complexes may be explained by a negative shift from E_0' caused by rapid homogeneous follow-up kinetics.[14] Thus, the reversible oxidation potentials of the two Pt complexes (+1.2 for MNT and +0.64 for TT) may be taken as representative for the thermodynamic oxidation potential. A comparison between the two series of complexes clearly shows that the redox potentials are governed by the ligands and not by the metal in each series.

The potentials of the first reduction and oxidation of these complexes may be related to the nature of the orbitals involved in these redox processes. In the case of the symmetric complexes (A), it is generally accepted that the ligand-localized $3b_{2g}$ orbital is the LUMO.[8-10] A corresponding assignment was made for some Ni(diimine)(dithiolate) complexes (B), where the $3b_{2g}$ orbital (in C_{2v} symmetry) is essentially a π^* orbital of the diimine.[12] Our results confirm this assignment. The cyclic voltammetry data (Table I) show that the first reduction of all six complexes, leading to the occupation of the LUMO by one electron, occurs at comparable potentials (∼−0.9 V). This is expected since all complexes contain the same diimine (BABA) as a common electron acceptor. The small variation of the reduction potential may reflect a small but variable amount of d-orbital character of the $3b_{2g}$ orbital.

There is, however, disagreement about the nature of the HOMO. In the case of the symmetric Ni complexes (A), it was suggested that the HOMO is the dithiolate-localized $2b_{1u}$[10] or a metal-centered d orbital.[8,9] In the mixed-ligand complexes (B) of nickel, it was assumed that a d orbital is the HOMO.[12] Our results suggest that for the complexes of the present study the HOMO is the dithiolate-based $2b_{1u}$ orbital.[15] The oxidation potential of these complexes shows a rather small variation with the metal. However, the oxidation potential depends very much on the nature of the dithiolate ligand. The complexes containing the TT^{2-} ligand are oxidized at potentials that are about 0.65 V lower than those of the corresponding MNT^{2-} compounds. This observation is not surprising since the electron-withdrawing nitrile substituents of MNT^{2-} stabilize the reduced ethylene-1,2-dithiolate form to a greater extent. Ni(BABA)(MNT) is the only complex that shows a deviation since it is oxidized at a lower potential (0.8 V) than the corresponding Pd and Pt complexes (∼1.20 V). As explained above, this deviation may not be caused by any differences in the electronic structure. As an alternative, however, it cannot be excluded presently that the HOMO of Ni(BABA)(MNT) is rather a d orbital.

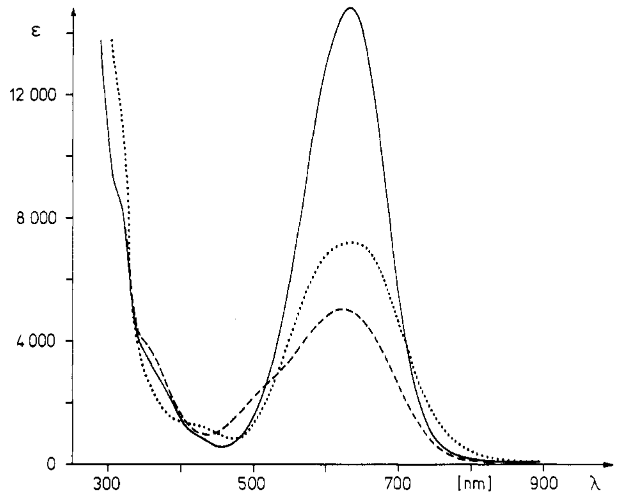

Figure 2. Electronic absorption spectra of M^{II}(BABA)(TT) with M = Ni (···), Pd (- - -), and Pt (—), dissolved in acetonitrile.

Electronic Spectra. The unique feature of the electronic spectra of all six complexes is an intense broad absorption band in the visible region (Figure 2, Table II). All complexes show a very strong negative solvatochromism. Dependent on the solvent polarity, the colors vary between red (polar) and blue (less polar) due to a shift of the visible absorption band (Table II).

The band in the visible, which is the longest wavelength absorption of all complexes, is assigned to the $2b_{1u} \rightarrow 3b_{2g}$ CT or IT transition from the reducing dithiolate to the oxidizing diimine ligand.[12,13] This band occurs also as intraligand transition in the symmetric complexes (A).[8-10,16] The spectra (Figure 2, Table II) show that the energy of the IT band does not vary very much with the metal. This observation adds further evidence in support of the assumption that the orbitals $2b_{1u}$ and $3b_{2g}$ are essentially ligand-localized orbitals without much participation of metal d orbitals. The IT band of the

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complexes M(BABA)(TT) appears at longer wavelengths than those of the compounds M(BABA)(MNT) since the $2b_{1u}$ orbital is stabilized more by MNT^{2-} than by the TT^{2-} ligand. These considerations show that the spectral data lead to the same conclusions as the results of the electrochemical measurements. It follows that the same orbitals, $2b_{1u}$ as HOMO and $3b_{2g}$ as LUMO, are involved in the redox processes as well as in the lowest energy optical transitions of these mixed-ligand complexes, with the possible exception of Ni(BABA)(MNT) (see above).

The strong negative solvatochromism of Ni(diimine)(dithiolate) compounds was already discussed by Miller and Dance.[12] Irrespective of the metal, all six complexes show roughly the same solvent dependence (Table II). The blue shift of the IT band with increasing solvent polarity suggests that the ground state is rather polar and stabilized by polar solvents. In the excited IT state, the dipole moment is apparently reduced. Consequently, polar solvents do not stabilize the excited state to the same extent.

For a correlation between the energies of optical metal-to-ligand CT transitions and solvent polarities, several empirical solvent parameters have been used,[17] e.g. Kosower Z or Reichardt E_T parameters.[18] Recently we used the expression $1/n^2 - 1/D$, where n^2 and D are the optical and static dielectric constants of the solvent.[11,19] This relationship was derived for IT transitions of weakly coupled redox centers without extensive electron delocalization.[3,20] Although this requirement may not be met for the ligand-based MV complexes, the qualitative correspondence seems to be as good as for the Z and E_T parameters.

Other Absorption Bands. While in the context of the present investigation, a discussion of absorption bands at higher energies is omitted as the nature of the long-wavelength band of M(diimine)(dithiolate) compounds requires some further comments. In most cases this band either is quite unsymmetric or shows a distinct shoulder (Figure 2, Table II). It seems to be composed of two bands. While the arguments presented above support the $2b_{1u} \rightarrow 3b_{2g}$ IT assignment for the longer wavelength component, the feature at higher energies may be of a different origin. Since it shows approximately the same solvent dependence as the lower energy band, it is certainly also of the CT type. We suggest that it is assigned to a CT transition from the lone pairs at the sulfur atoms of the dithiolate to the π^* orbital ($3b_{2g}$) of the diimine ligand. This assumption is supported by a recent observation that the complex (biacetyl bis(mercaptoethylimine))nickel(II) exhibits also a strong negative solvatochromism, which is caused by the solvent-dependent shift of the visible absorption band.[19] In this case the tetradentate ligand coordinates to nickel via a 1,2-diimine unit and two sulfur atoms, which, however, are not part of an ethylene-1,2-dithiolate structure. The low-energy absorption of this complex was assigned to the sulfur-to-diimine CT transition. In the spectra of the symmetric nickel complexes (A), such a sulfur-to-$2b_{2g}$ absorption occurs at slightly higher energies than the $2b_{1u} \rightarrow 3b_{2g}$ band.[8-10] In the symmetric compounds these transitions are, of course, not of the CT type.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. Biacetyl bis(anil)-(BABA)[21] and disodium disulfidomaleonitrile $Na_2[S_2C_2(CN)_2]$ (Na_2MNT)[22] were prepared by published procedures. Toluene-3,4-dithiol (H_2TT) was obtained from Eastman Organic Chemicals. The complexes $Ni(BABA)_2Cl_2$,[21,23] Ni(BABA)(MNT),[12] and Pd(benzonitrile)$_2$Cl$_2$[24] were synthesized by literature methods.

Electronic absorption spectra were recorded on a Varian Techtron Super Scan 3 recording spectrophotometer. For spectroscopy, solvents were spectrograde. Cyclic voltammetry experiments were performed on a Princeton Applied Research (PAR) Model 170 electroanalytical system using a three-electrode configuration and a conventional two-compartment cell. A platinum-disk working electrode and a SCE reference electrode were employed with use of a salt bridge. The measurements were carried out in CH_3CN as solvent, which was vacuum-line distilled from P_4O_{10} and degassed by several freeze–thaw cycles. The supporting electrolyte was $(n\text{-}Bu_4N)ClO_4$.

Pd(BABA)(MNT). To a solution of 0.95 g of Pd(benzonitrile)$_2$Cl$_2$ in 100 mL of CH_2Cl_2 was added a solution of 0.6 g of BABA in 100 mL of CH_2Cl_2. The resulting solution was boiled for a few seconds. After addition of 0.45 g of Na_2MNT, the mixture was heated under reflux for 2 h. The hot mixture was filtered and concentrated by evaporation to 50 mL. Upon addition of 200 mL of ether, a dark red precipitate formed. It was collected by filtration, washed with ether, and dried under vacuum. For further purification this material was dissolved in 100 mL of hot acetone and filtered. The deep purple solution was concentrated to 40 mL. To the hot solution of acetone was slowly added 150 mL of warm ether. After refrigeration for 12 h, the dark blue crystals obtained were collected by filtration and dried under vacuum; yield 0.11 g (~12%). Anal. Calcd for $C_{20}H_{16}N_4PdS_2$: C, 49.74; H, 3.34; N, 11.60. Found: C, 49.65; H, 3.46; N, 11.65.

Pt(BABA)(MNT). A mixture of 1.5 g of Na_2PtCl_4 and 1.5 g of BABA was finely ground in a mortar. In a test tube this mixture was heated on an oil bath at 170 °C for 20 min. The reaction product was cooled and suspended in 80 mL of CH_2Cl_2. After addition of 1 g of Na_2MNT, the suspension was stirred for 4 h. The solution turned dark blue. After filtration the yellow-brown residue was washed three times with 10 mL of CH_2Cl_2. Upon addition of 500 mL of hexane to the combined filtrates, a deep purple precipitate formed. It was collected by filtration and purified twice by dissolution in CH_2Cl_2 and chromatography on Al_2O_3. The eluted dark blue solution was concentrated by evaporation to 10 mL. After the solution was allowed to stand at 0 °C for 1 h, the red-violet crystals were filtered and dried under vacuum; yield 0.09 g (~5%). Anal. Calcd for $C_{20}H_{16}N_4PtS_2$: C, 42.03; H, 2.82; N, 9.80. Found: C, 41.96; H, 2.76; N, 9.78.

Ni(BABA)(TT)·0.3CH$_2$Cl$_2$. To a solution of 0.6 g of Ni(BABA)$_2$Cl$_2$ in 50 mL of ethanol was added 0.16 g of H_2TT with stirring. A dark blue precipitate was formed. It was collected by filtration and dried under vacuum. The crude product was purified by dissolution in 50 mL of CH_2Cl_2 and reprecipitation upon addition of 250 mL of ether. The dark violet crystals were collected by filtration, washed with ether, and dried under vacuum. The product was obtained as dichloromethane solvate; yield 0.22 g (~49%). Anal. Calcd for $C_{23}H_{22}NiN_2S_2$ $(+0.3CH_2Cl)_2$: C, 58.95; H, 4.79; N, 5.90. Found: C, 59.06; H, 4.61; N, 5.67.

Pd(BABA)(TT). A solution of 0.19 g of Pd(benzonitrile)$_2$Cl$_2$ in 80 mL of CH_2Cl_2 was added to a solution of 0.12 g of BABA in 30 mL of CH_2Cl_2 with stirring. Upon addition of 0.08 g of H_2TT, the solution turned dark green. It was immediately chromatographed twice on Al_2O_3. Deep purple crystals were obtained by slow evaporation of the solvent; yield 0.03 g (~11%). Anal. Calcd for $C_{23}H_{22}N_2PdS_2$: C, 55.58; H, 4.40; N, 5.63. Found: C, 55.49; H, 4.37; N, 5.63.

Pt(BABA)(TT). A mixture of 1.14 g of Na_2PtCl_4 and 1.14 g of BABA was finely ground and then heated in a test tube on an oil bath at 170 °C for 20 min. The reaction product was cooled and added to a solution of 0.66 g of H_2TT in 100 mL of CH_2Cl_2. This mixture was stirred for 4 h. After filtration, the residue was washed three times with 10 mL of CH_2Cl_2. The combined filtrates were chromatographed on Al_2O_3 with CH_2Cl_2. The eluted solution was concentrated by evaporation to 40 mL. After addition of 300 mL of ether and evaporation to 200 mL, the solution was filtered. The filtrate

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was concentrated by evaporation to 130 mL. Upon addition of 500 mL of hexane, a dark blue precipitate formed. It was collected by filtration and dried under vacuum; yield 0.15 g (~8%). Anal. Calcd for $C_{23}H_{22}N_2PtS_2$: C, 47.16; H, 3.78; N, 4.78. Found: C, 46.95; H, 3.97; N, 4.59.

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Registry No. Ni(BABA)(MNT), 42593-96-4; Pd(BABA)(MNT), 88287-58-5; Pt(BABA)(MNT), 88271-97-0; Ni(BABA)(TT), 88271-98-1; Pd(BABA)(TT), 88271-99-2; Pt(BABA)(TT), 88272-00-8.

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Alcohol Formation from *O*-Alkyl Aldoximes by Reaction with Ruthenium(II) Complexes[1]

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A potentially useful goal of transition-metal chemists is the development of processes whereby one or more metal centers can catalyze the production of alcohols from small organic or gaseous substrates.[2] We report one of the few examples in which an alcohol is produced at a Ru(II) center by a Ru(II)-promoted ligand reaction without a concomitant net redox change on the metal or ligand.[3] The reaction occurs when freshly generated $Ru(NH_3)_5H_2O^{2+}(aq)$ reacts with *O*-alkyl aldoximes and has the overall stoichiometry

$$(NH_3)_5RuH_2O^{2+}(aq) + RON{=}C(H)R' \rightarrow (NH_3)_5RuN{\equiv}CR'^{2+} + ROH \quad (1)$$

where R = CH_3 or C_2H_5 and R' = CH_3 or C_6H_5.

One feature of potential importance in this system is that both the *O*-alkyl group and the activated hydrogen needed for alcohol production are poised on the same ligand.

Experimental Section

Deionized water (Continental Water) was distilled from alkaline permanganate before use. $[Ru(NH_3)_5Cl]Cl_2$ was prepared according to literature procedures[4] from $RuCl_3{\cdot}3H_2O$ (Engelhard Industries). O-alkylated aldoximes were prepared by reacting the corresponding aldehydes with either methoxyamine hydrochloride (Aldrich Chemical Co.) or ethoxyamine hydrochloride (Eastman Kodak).[5,6] The aldoximes were vacuum distilled and were analyzed for purity by gas chromatography;[7] their identity was verified by mass spectrometry.

Table I. Comparison of Spectral Properties of Ruthenium Products Isolated from the Reaction of $Ru(NH_3)_5H_2O^{2+}$ with RON=CHR'

		ν(C≡N), cm^{-1}		λ_{max}, nm (log ϵ)	
R[a]	R'	lit.[b]	found[c]	lit.[b]	found[d]
CH_3	CH_3	2239[e]	2246	229 (4.19)	229 (4.17)
CH_3	C_6H_5	2188[f]	2185	376 (3.93)	376 (3.93)
C_2H_5	CH_3	2239[e]	2246	229 (4.19)	229 (4.16)
C_2H_5	C_6H_5	2188[f]	2185	376 (3.93)	376 (3.93)

[a] Alcohol reaction products were detected by GC and ^1H NMR in filtrate: first two listings, CH_3OH; last two listings, C_2H_5OH. [b] From ref 9. [c] PF_6^- salt, Nujol mull; differences in ν(C≡N) are seen as in ref 9b according to the counterion used. [d] ϵ in M^{-1} cm^{-1}; average of five determinations per compound. [e] BF_4^- salt. [f] ClO_4^- salt.

All other chemicals were of reagent grade and were obtained from Aldrich Chemical Co. All manipulations were carried out under an argon atmosphere at room temperature. In a typical reaction, 100 mg (0.34 mmol) of $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5.0 mL of distilled deionized water, and the resultant mixture was degassed by bubbling Ar through the solution via a syringe needle for 15 min. The Ru^{3+} solution was converted to $Ru(NH_3)_5H_2O^{2+}(aq)$ by base hydrolysis followed by reduction over Zn amalgam for 45 min.[8] The Zn amalgam was then removed by filtration because alkylzinc reagents in tetrahydrofuran have been reported to catalyze the room-temperature conversion of benzaldehyde *O*-ethyloxime to the corresponding nitrile over the course of more than 15 h.[6a] A 4-10 molar excess of *O*-alkyl aldoxime was added to the stirred $Ru(NH_3)_5H_2O^{2+}$ solution under Ar. The reaction was allowed to continue for approximately 30 min or until an aliquot of the reaction mixture showed no further changes in the UV-visible region of the electronic spectrum. The reaction mixture was then filtered onto solid KPF_6, whereupon a yellow solid precipitated immediately. The solid was isolated by filtration; the reaction filtrate was treated separately as described below. The solid product was washed successively with ethanol and diethyl ether and was dried in vacuum at room temperature over P_2O_5 overnight. The amounts of ruthenium products isolated ranged from 65-80% of the theoretical yields. Alcohols were detected in the reaction filtrate by both gas chromatography and ^1H NMR. GC samples were obtained directly from the reaction solutions, after precipitation of the Ru(II) compounds with KPF_6, followed by filtration. No alcohol was detected when only *O*-alkyl aldoxime samples were injected into the GC. ^1H NMR samples were prepared by extraction of the reaction filtrate with CD_2Cl_2. Solid products were characterized by infrared absorption spectroscopy (Beckman 4210) and UV-visible absorption spectroscopy (Cary 210 or 219). Gas chromatograms were obtained on a Varian Series 1400 GC (thermal conductivity detector, Poropak Q column) and ^1H NMR spectra on a Varian EM 360 spectrometer (CD_2Cl_2 solvent; tetramethylsilane, internal standard). Mass spectra of the aldoximes were run on a Finnigan 4021C GC/MS. Microanalyses were provided by Robertson Laboratories, Florham Park, NJ.

Results

UV-Visible Absorption Properties. Addition of *O*-alkyl aldoximes to an aqueous solution of $Ru(NH_3)_5H_2O^{2+}$ leads to a color change that is complete within about 30 min. The UV-visible absorption spectra of the reaction solutions containing $RON{=}CHCH_3$ displayed an absorption maximum at 229 nm, while the solutions derived from the reactions containing $RON{=}CHC_6H_5$ showed an absorption maximum at 376 nm. No spectral intermediates were detected during the course of the reactions. The electronic spectra of 10^{-4}-10^{-5} M aqueous solutions of the isolated solids displayed peaks corresponding to the analogous pentaammineruthenium(II)-nitrile compounds.[9] The observed spectra were in good agreement with those of the reaction solutions prior to product isolation.

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(1) Paper presented in part at the 34th Southeast Regional American Chemical Society Meeting, Birmingham, AL, Nov 1982, and the 56th Annual Meeting of the South Carolina Academy of Sciences, Columbia, SC, Mar 1983.

(2) For some recent reviews and examples see: (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

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(7) *O*-Alkyl aldoximes can exist in both *E* and *Z* isomers. For our purposes in this study, the *E* and *Z* isomers were not separated.

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