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N-(2-Pyridyl)acetamide Complexes of Palladium(II), Cobalt(II), Nickel(II), and Copper(II)

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N-(2-Pyridyl)acetamide (aapH) complexes of palladium(II), cobalt(II), nickel(II), and copper(II) have been studied by means of magnetic susceptibilities, and infrared, electronic, and PMR spectra. In the octahedral complexes $M(aapH)_2X_2$(M = Co, Ni, Cu; X = Cl, Br, NCS, NO_3), bidentate aapH is chelated through the pyridine-N and amide-O atoms, whereas in the square-planar $Pd(aapH)_2X_2$ (X = Cl, Br) unidentate aapH is coordinated through the pyridine-N atom alone. Under alkaline conditions aapH is deprotonated in the presence of palladium(II) to form $Pd(aap)_2 \cdot 4H_2O$, aap being an anionic bidentate ligand and chelating through the pyridine-N and amide-O atoms.

Introduction

An acid amide group has two donor atoms, nitrogen and oxygen, and it depends upon experimental conditions which one of them coordinates to metal ions. We have studied complexes[1–4] of various acid amides and found the coordination through an oxygen or a deprotonated nitrogen atom of primary acid amides, which has been confirmed by X-ray analysis.[4] Other authors also obtained the similar results.[5–11] Some authors, however, have reported the complexes of primary acid amides, for which the coordination of a non-deprotonated amide-N atom is claimed.[12–14] Recently another example of the N-coordination of non-deprotonated secondary acid amides was reported.[15] To elucidate this point we have studied the complexes of a secondary acid amide, N-(2-pyridyl)acetamide (abbreviated as aapH), and found the O-coordination of the ligand, which agrees with our previous conclusion.[1–4]

Experimental

Preparation of the Ligand aapH

One mol of 2-aminopyridine was refluxed with one mol of acetic anhydride for two hours. The product was distilled under vacuum (155–158 °C/23 mmHg) and recrystallized from a mixture of benzene and n-hexane to give white crystals (m.p. 60–62 °C). The yield was 90%. Found: C, 61.90; H, 5.53; N, 20.56%. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.67%. The deuterated ligand, aapD, was prepared by recrystallizing aapH from D_2O.

Preparation of the Complexes

$Co(aapH)_2X_2$ (X = Cl, Br, NO_3, NCS), $Ni(aapH)_2X_2$ (X = Cl, Br, NO_3, NCS), and $Cu(aapH)_2X_2$ (X = Cl, Br, NO_3)

To an ethanolic solution (30 ml) of an appropriate metal salt(3 mmol) was added an ethanolic solution (20 ml) of aapH(6 mmol) at room temperature. The precipitate was washed with ethanol and dried in air. The yield was almost quantitative.

$Co(aapH)_2(NCS)_2$ is reddish violet when prepared below 5 °C, while it is light brown when prepared at room temperature. The reddish violet isomer can be converted to the light brown isomer when an ethanolic suspension of the former is heated for a few hours.

$Pd(aapH)_2X_2$ (X = Cl, Br)

To a hot ethanolic solution (50 ml) of lithium tetrachloropalladate which had been prepared from palladium chloride (0.5 g) and lithium chloride (0.3 g) *in situ*, was added a hot ethanolic solution (30 ml) of aapH (0.8 g) under vigorous stirring. Fine crystals precipitated were washed with ethanol and dried in air. The yield was 0.75 g. The bromide was prepared in a similar way using lithium bromide (1.2 g). The yield was 0.95 g.

$Pd(aap)_2 \cdot 4H_2O$

To a suspension of $Pd(aapH)_2Cl_2$ (0.75 g) in 80 ml of ethanol was added an aqueous solution (20 ml) of potassium hydroxide (0.4 g). The mixture became clear and yellow crystals precipitated. The product was washed with water and dried in air to give 0.6 g.

Under alkaline conditions deprotonation of aapH was facilitated only by palladium(II), and thus Pd $(aap)_2 \cdot 4H_2O$ was formed. Nickel, cobalt, and copper precipitated their hydroxides under the same conditions without forming complexes.

Measurements

The measurements of infrared, electronic, and PMR spectra, and magnetic susceptibilities were carried out as described previously.[16, 17]

Results and Discussion

The analytical data for the complexes prepared and their colours are shown in Table I.

Magnetic Moments

The three palladium complexes are diamagnetic (Table II) and seem to have square-planar structures, while all the other complexes have typical values of high-spin complexes.[18]

Electronic Spectra

The electronic spectra of all the copper complexes are characteristic of distorted octahedral copper(II). The spectra of $\mathrm{Cu(aapH)_2X_2}$ ($\mathrm{X = Cl, Br, NO_3}$) depend slightly upon the anions to show their weak coordination (Table II).

The spectrum of $\mathrm{Ni(aapH)_2(NCS)_2}$ is typical of octahedral nickel(II) complexes. As the spectrum of the complex is appreciably different from that of *trans*-$\mathrm{[Ni(mepiaH)_2(NCS)_2]}$, where mepiaH is N-methylpicolinamide[16] (Formula I)*, its structure may be different. The bands of $\mathrm{Ni(aapH)_2X_2}$ ($\mathrm{X = Cl, Br, NO_3}$) can be assigned on the basis of a D_{4h} symmetry (Formula I).[19]

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* In Formula I N–O represents a chelate ring formed of pyridine-N and amide-O atoms.

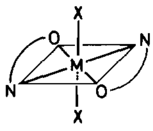
TABLE I. Colours and Analytical Data for the Complexes.

Complex	Colour	M % (Calcd.)	N % (Calcd.)	Other	% (Calcd.)
$\mathrm{Cu(aapH)_2Cl_2}$	Bluish green	15.70(15.62)	13.76(13.77)	Cl	17.41(17.43)
$\mathrm{Cu(aapH)_2Br_2}$	Bluish green	13.06(12.82)	11.38(11.30)	Br	32.47(32.24)
$\mathrm{Cu(aapH)_2(NO_3)_2}$	Blue	13.94(13.82)	18.24(18.27)		
$\mathrm{Ni(aapH)_2Cl_2}$	Bluish green	14.50(14.61)	13.93(13.94)	Cl	17.53(17.64)
$\mathrm{Ni(aapH)_2Br_2}$	Bluish green	11.96(11.96)	11.30(11.42)	Br	32.17(32.56)
$\mathrm{Ni(aapH)_2(NO_3)_2}$	Bluish violet	12.85(12.90)	18.09(18.47)		
$\mathrm{Ni(aapH)_2(NCS)_2}$	Bluish violet	13.03(13.13)	18.46(18.79)	NCS	25.73(25.98)
$\mathrm{Co(aapH)_2Cl_2}$	Purple	14.67(14.66)	13.69(13.93)	Cl	17.64(17.63)
$\mathrm{Co(aapH)_2Br_2}$	Purple	11.95(12.00)	11.69(11.41)	Br	32.50(32.54)
$\mathrm{Co(aapH)_2(NO_3)_2}$	Orange	12.75(12.94)	18.64(18.46)		
rv-$\mathrm{Co(aapH)_2(NCS)_2}$	Reddish violet	12.96(13.17)	18.71(18.78)	NCS	25.29(25.97)
lb-$\mathrm{Co(aapH)_2(NCS)_2}$	Light brown	13.12(13.17)	18.62(18.78)	NCS	25.66(25.97)
$\mathrm{Pd(aapH)_2Cl_2}$	Light yellow	23.43(23.66)	12.33(12.46)	Cl	15.56(15.77)
$\mathrm{Pd(aapH)_2Br_2}$	Yellowish brown	19.83(19.76)	10.46(10.40)	Br	29.55(29.68)
$\mathrm{Pd(aap)_2 \cdot 4H_2O}$	Yellow	23.74(23.71)	12.60(12.49)	$\mathrm{H_2O}$	16.04(16.06)

TABLE II. Magnetic Moments and Diffuse Reflectance Spectra.

Complex	μ_{eff} B.M.	Absorption maximum in 10^3 cm^{-1}
$\mathrm{Cu(aapH)_2Cl_2}$	1.88	10.7sh, 15.5, 27.0sh[a]
$\mathrm{Cu(aapH)_2Br_2}$	1.89	10.5sh, 15.5, 26.0sh
$\mathrm{Cu(aapH)_2(NO_3)_2}$	1.88	11.3sh, 15.8, 27.0sh
$\mathrm{Ni(aapH)_2Cl_2}$	3.23	8.1, 10.8sh, 15.6, 24.8
$\mathrm{Ni(aapH)_2Br_2}$	3.17	7.6, 11.1sh, 13.0w, 15.8, 24.4
$\mathrm{Ni(aapH)_2(NO_3)_2}$	3.15	8.8, 10.7sh, 16.2, 26.5sh
$\mathrm{Ni(aapH)_2(NCS)_2}$	3.21	10.3, 17.0, 26.7
$\mathrm{Co(aapH)_2Cl_2}$	5.02	8.6, 14.8, 15.8, 17.5, 18.8, 19.8, 21.0sh, 27.5sh
$\mathrm{Co(aapH)_2Br_2}$	5.02	8.6, 14.5sh, 17.4, 18.4, 19.2, 22.3, 28.0sh
$\mathrm{Co(aapH)_2(NO_3)_2}$	4.98	9.1, 20.6br, 27.5sh
rv-$\mathrm{Co(aapH)_2(NCS)_2}$	4.94	8.7, 19.0, 20.3sh, 32.0
lb-$\mathrm{Co(aapH)_2(NCS)_2}$	4.98	9.5, 11.3sh, 20.2br, 29.5sh
$\mathrm{Pd(aapH)_2Cl_2}$	Dia.[b]	24.9
$\mathrm{Pd(aapH)_2Br_2}$	Dia.	23.9
$\mathrm{Pd(aap)_2 \cdot 4H_2O}$	Dia.	27.0sh

[a] sh = shoulder, w = weak, and br = broad. [b] Dia. = diamagnetic.

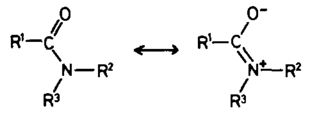


I

The spectrum of $Co(aapH)_2(NO_3)_2$ is characteristic of octahedral cobalt(II). For $Co(aapH)_2X_2$ (X = Cl, Br) several bands are found in the region $14–22 \times 10^3$ cm^{-1} where two bands due to the transitions $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ and $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ are expected. The splitting may be caused by the ligand field of low symmetry as well as by spin–orbit coupling.[19] The spectrum of the reddish violet $Co(aapH)_2(NCS)_2$ resembles that of *trans*-$[Co(mepiaH)_2(NCS)_2]$ (Formula I),[16] suggesting their similar structures, whereas the light brown isomer shows an appreciably different spectrum and its structure is not clear yet.

Infrared Spectra

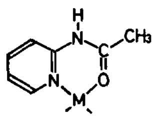
The spectrum of free aapH was measured in a dilute chloroform solution to obtain the data of a monomeric amide (Table III). A free acid amide has the following resonance structures[20,21] with predominant



II III

Formula II. On coordination through its oxygen atom, the contribution of Formula III increases. If coordination occurs through the nitrogen atom, its hybridization will be sp^3 and the C=O bond will become a complete double bond with loss of the resonance energy.[21]

The amide I band (Table III) consists mainly of $\nu(C=O)$, and the amide II and III bands arise from $\nu(C–N)$ as well as from $\delta(N–H)$, although these modes are coupled to one another.[22] Consequently for an amide group coordinated through the oxygen atom, the amide I band will shift to a lower frequency and the amide II and III bands to higher frequencies. On the other hand, if the amide-nitrogen atom coordinates, the amide I, II, and III bands should shift to the opposite directions. Our experimental data revealed that the amide bands of all the cobalt, nickel, and copper complexes studied shifted towards the directions expected for the amide-oxygen coordination (Formula IV, Table III):



IV

TABLE III. Infrared Spectral Bands due to the Amide Groups of the Ligand and Complexes (cm^{-1}).

Compound	ν(N–H)	Amide		
		I	II	III
aapH	3183	1693	1531	1242
aapH($CDCl_3$)	3205	1697	1515	1234
	3265			
aapD[a]	2295	1679	1395	972
$Cu(aapH)_2Cl_2$	2872	1645	1537	1346
	2814	1610		
	2782			
$Cu(aapD)_2Cl_2$	2205	1616	1410	1096
	2195			
	2100			
$Ni(aapH)_2Cl_2$	2980	1671	1537	1340
		1619		
$Ni(aapD)_2Cl_2$	2280	1648	1409	1001
$Pd(aapH)_2Cl_2$	3275	1712	1512	1234
$Pd(aapD)_2Cl_2$	2423	1703	1386	971
$Pd(aap)_2 \cdot 4H_2O$	[b]	1568	1393	[b]
		1510		

[a] Deuterated ligand, C_5H_4N-$NDCOCH_3$. [b] These bands disappeared.

For $Pd(aapH)_2X_2$ (X = Cl, Br) the amide I band shifted slightly to a higher frequency, while the the amide II and III bands remained practically in the same positions, indicating the non-coordination of the amide group. The slight shifts of $\nu(N–H)$ and of the amide I band on coordination may be due to the different hydrogen-bonding between free and complexed aapH.

The spectra of $Co(aapH)_2(NO_3)_2$ and $Ni(aapH)_2(NO_3)_2$ indicate coordination of NO_3 ions, whereas in $Cu(aapH)_2(NO_3)_2$ the anion seems to be not strongly coordinated. The NCS groups in $Co(aapH)_2(NCS)_2$ and $Ni(aapH)_2(NCS)_2$ seem to be coordinated with the nitrogen atom, since $\nu(C \equiv N)$, $\nu(C–S)$, and $\delta(NCS)$ are observed in the regions expected for the nitrogen-coordination (Table IV).

TABLE IV. Infrared Spectra of the Thiocyanato Complexes (cm^{-1}).

Complex	$\nu C \equiv N$	$\nu C–S$	δNCS	$\nu M–N$
$Ni(aapH)_2(NCS)_2$	2115	789sh[a]	476	268
	2103sh		468sh	248
rv-$Co(aapH)_2(NCS)_2$	2093	790	478	278
			472	
lb-$Co(aapH)_2(NCS)_2$	2106br	792	474	249
			466	233

[a] sh = shoulder; br = broad.

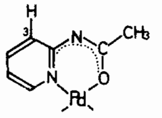
TABLE V. Selected Bands of Far Infrared Spectra (cm^{-1}).

Compound	Amide		Pyridine Bands	
	IV	VI		
aapH	677	556	625	414
aapD	675	553	625	414
$Cu(aapH)_2Cl_2$	696	598	653	434
$Cu(aapD)_2Cl_2$	695	594	653	434
$Ni(aapH)_2Cl_2$	695	582	646	434
$Ni(aapD)_2Cl_2$	693	579	646	434
$Co(aapH)_2Cl_2$	693	575	643	427
$Pd(aapH)_2Cl_2$	683	554	655	457
$Pd(aapD)_2Cl_2$	677	553	655	457
$Pd(aap)_2 \cdot 4H_2O$	633	530	653	459

Far Infrared Spectra

In all the complexes studied coordination of the pyridine ring is shown by the higher frequency shift of its deformation bands at 625 and 414 cm^{-1} (TableV). Characteristic bands of an acid amide in this region are the amide VI and IV bands.[22] The amide VI band is mainly due to the deformation mode of an amide group. Its shift to a higher frequency on coordination with cobalt, nickel, and copper indicates the amide-oxygen coordination.[23] On the other hand, in Pd $(aapH)_2X_2$ (X = Cl, Br), the amide VI and IV bands scarcely shift to show non-coordination of the amide group (Table V).

The two amide bands, VI and IV, of the deprotonated complex $Pd(aap)_2 \cdot 4H_2O$ shift to lower frequencies (Table V), and the amide I band is observed at a very low frequency, suggesting the mode of coordination to be as shown in Formula V, in which the chelate ring is similar to that of β-diketone complexes. This structure is further supported by the disappearance of ν(N–H) and the presence of a band at 291 cm^{-1} which is close to the band of $Pd(acac)_2$* observed at 294 cm^{-1} and assignable to ν(Pd–O).[24]



V

Concerning ν(M–X) bands, $Pd(aapH)_2Cl_2$ and $Pd(aapH)_2Br_2$ show a strong band at 346 and 259 cm^{-1}, respectively, which is in the region[25] diagnostic of ν(Pd–X) of *trans*-$[PdL_2X_2]$. Thus these two palladium complexes seem to be square-planar, the two aapH ligands being mutually in the *trans* positions. They are coordinated through the pyridine-nitrogen atom alone without coordination of the amide group.

From comparison of the far infrared spectra of $M(aapH)_2X_2$ (M = Co, Ni; X = Cl, Br, NCS, NO_3), tentative assignments of ν(M–X) are possible and the values of ν(M–NCS) are given in Table IV. The position of ν(M–NCS) of *rv*-$Co(aapH)_2(NCS)_2$ is close to that of *trans*-$[Co(mepiaH)_2(NCS)_2]$,[16] suggesting a closely related structure (Formula I, X = NCS). Resemblance of the spectra of $Ni(aapH)_2(NCS)_2$ and *lb*-$Co(aapH)_2(NCS)_2$ shows that these two have a similar structure, and the appearance of two ν(M-NCS) bands at different positions from those of the above *rv*-isomer may suggest a *cis*-arrangement of two NCS groups, which is supported by the splitting or broadening of ν(C≡N) bands. The above assumptions are compatible with the electronic spectral results. Co $(aapH)_2Cl_2$ and $Ni(aapH)_2Cl_2$ show ν(M–Cl) at 200 and 205 cm^{-1}, respectively, in the range indicative of six-coordination.[25]

From the above spectral data, $Co(aapH)_2X_2$, Ni $(aapH)_2X_2$, and $Cu(aapH)_2X_2$ (X = Cl, Br, NO_3) are concluded to have a structure like Formula I.

PMR Spectra

Free aapH in $CDCl_3$ shows a singlet at δ = 2.22 ppm (CH_3), three multiplets at 7.03(pyridine ring 5-H), 7.69(4-H), and 8.30(3,6-H), and a broad singlet at 10.44(amide N-H). The spectrum is quite similar to that [26] of aapH in CCl_4. Only $Pd(aap)_2 \cdot 4H_2O$ is sufficiently soluble in $CDCl_3$ to measure the PMR spectrum. The spectrum shows a singlet at 2.25 ppm(CH_3), a complex multiplet at 6.99(3,5-H), a multiplet at 7.69(4-H), and a double doublet at 8.49(6-H). The broad singlet of the free ligand at 10.44(N-H) disappears on coordination and this is consistent with the disappearance of ν(N–H) in the infrared spectrum. When an appropriate amount of a shift reagent, Eu $(dpm)_3$* is added, the induced shifts (Δ) observed for both the CH_3 (Δ = 1.67 ppm) and the 3-H (Δ = 1.59) are much larger than those of the other peaks which are less than 0.65 ppm. Since the magnitude of the induced shifts is roughly inversely proportional to the cube of the distance between the hydrogen in question and the europium atom,[27] the europium atom must be close to both the CH_3 and the 3-H, and consequently to the deprotonated amide-nitrogen atom (FormulaV). No structure other than Formula V can explain satisfactorily the induced shifts, and this conclusion is also borne out by the infrared spectral studies.

Mode of Coordination of an Acid Amide Group

The free acid amide group has a planar structure with certain resonance stabilization energy.[21] The amide-nitrogen coordination without deprotonation will change the sp^2 hybridization of the nitrogen atom into an sp^3 hybridization with loss of the stabilization energy

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* acac = acetylacetonate anion.

* $Eu(dpm)_3$ = tris(dipivaloylmethanato)europium(III).

as well as the planar structure. On the other hand, the amide-oxygen coordination will require only the donation of a lone pair of electrons to a metal without change in hybridization and loss of the resonance energy. Therefore, oxygen-coordination is more favoured than nitrogen-coordination for a non-deprotonated acid amide group. The result of the present study as well as our results[1–4] obtained so far for various acid amide complexes support completely the above view.

Hughes and Rutt[15] have studied the copper(II) complexes of 2-acetamido-thiazole and -benzothiazole, and concluded that the non-deprotonated amide-nitrogen atoms are coordinated to copper(II). The evidences presented, however, seem to be insufficient in view of the above discussions based on our results. As the evidences they presented the increase in the intensity of ν(N–H) of amide groups and scarce shift of the amide I band to a lower frequency, but a similar change on coordination was found by us for $Pd(aapH)_2X_2$ (X = Cl, Br), in which aapH is coordinated only through the pyridine ring-nitrogen atom without coordination of the amide group. The electronic spectra reported[15] for CuL_2Cl_2 (L = 2-acetamido-thiazole and -benzothiazole) are similar to those of polymeric halogen-bridged CuL_2Cl_2 (L = a heterocyclic nitrogen donor)[28] and may be better explained by polymeric structures. Thus for the complexes of the thiazole derivatives it may be more appropriate to assume the coordination through the ring-nitrogen alone than to assume the coordination of the non-deprotonated amide-nitrogen atom.

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References

1 M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, 25A,* 365 (1969).

2 M. Sekizaki and K. Yamasaki, *Inorg. Chim. Acta, 4,* 296 (1970) and references therein.

3 M. Nonoyama, S. Kitagawa, and K. Yamasaki, *Nippon Kagaku Zasshi, 92,* 839 (1971).

4 M. Sekizaki, *Acta Cryst., B29,* 327 (1973), and references therein.

5 D.H. Brown, R.D. Burbank, and M.B. Robin, *J. Am. Chem. Soc., 91,* 2895 (1969).

6 D.H. Brown, D.R. MacSween, M. Mercer, and D.W.A. Sharp, *J. Chem. Soc. (A), 1971,* 1574.

7 M.A. Pellinghelli, A. Tiripicchio, and M.T. Camellini, *Acta Cryst., B28,* 998 (1972) and references therein.

8 M.L. Schneider, G. Ferguson, and R.J. Balahura, *Can. J. Chem., 51,* 2180 (1973).

9 M. Wicholas and R.S. Drago, *J. Am. Chem. Soc., 91,* 5963 (1969) and references therein.

10 J. Reedijk, *Inorg. Chim. Acta, 5,* 687 (1971).

11 J.M. Gioria and B.P. Susz, *Helv. Chim. Acta, 54,* 2251 (1971).

12 M.F. Farona, J.G. Grasselli, H. Grossman, and W.M. Ritchey, *Inorg. Chim. Acta, 3,* 495, 503 (1969).

13 K.H. Shaw and G.J. Sutton, *Aust. J. Chem., 22,* 1835, 1841 (1970).

14 A. Solladié–Cavallo and M. Mascarell, *J. Chim. Phys., 67,* 1345 (1970).

15 M.H. Hughes and K.J. Rutt, *J.C.S. Dalton, 1972,* 1311.

16 M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 3,* 585 (1969).

17 M. Nonoyama, Y. Tomomoto, and K. Yamasaki, *Nippon Kagaku Kaishi, 1972,* 562.

18 E.K. Barefield, D.H. Busch, and S.M. Nelson, *Quart. Rev., 22,* 457 (1969).

19 A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1968), p. 249.

20 M.B. Robin, F.A. Bovey, and H. Basch, "The Chemistry of Amides", ed by J. Zabicky, Interscience, London (1970), p. 1.

21 J.D. Roberts and M.C. Caserio, "Basic Principles of Organic Chemistry", Benjamin, New York (1965), p. 674.

22 T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys., 29,* 611 (1958).

23 G. Durgaprasad, D.N. Sathyanarayana, and C.C. Patel, *Spectrochim. Acta, 28A,* 2311 (1972).

24 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd. ed., Wiley-Interscience, New York (1970), p. 247.

25 D.M. Adams, "Metal–Ligand and Related Vibrations", Edward Arnold, London (1967), p. 26.

26 R.F.C. Brown, L. Radon, S. Sternhell, and I.D. Rae, *Can. J. Chem., 46,* 2577 (1958).

27 W.DeW. Horrocks, Jr. and J.P. Sipe, III, *J. Am. Chem. Soc., 93,* 6800 (1971).

28 W. Ludwig and F. Gasser, *Helv. Chim. Acta, 52,* 107 (1969).