the 95% confidence limits) was 2.5×10^{-3} M^{-1} $\sec^{-1}$. The actual value of k_1 is too small to determine accurately and could well be several orders of magnitude smaller than the upper limit given. Comparison of other pentaammine systems[11] shows that k_1 for chromium(III) is generally about $^1/_{100}$ times as great as for cobalt(III). Therefore k_1 is estimated to be about 2×10^{-4} M^{-1} $\sec^{-1}$ for $(NH_3)_5CrO_2C_2F_3^{2+}$ based on the analogous rate constant for $(NH_3)_5CoO_2C_2F_3^{2+}$.[2a]

A term second order in hydroxide ion has been observed for several carboxylatopentaamminecobalt(III)[2a,3] and -rhodium(III)[2b] complexes. The ^{18}O tracer work of Jordan and Taube[2a] has shown that this hydrolysis path involves carbon-oxygen bond breaking in $(NH_3)_5CoO_2C_2F_3^{2+}$. Subsequent kinetic studies[3] have shown that this reaction is quite sensitive to the carboxylate ligand and insensitive to the metal ion. The activation parameters for the alkaline hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$ confirm this generalization when compared to previous results (see Table IV). The mechanism of this reaction, as discussed previously,[2a] is thought to involve the concerted attack of two hydroxide ions, one making a bond with the acyl carbon atom of the ligand and the second removing a proton from the first. The process is considered to be concerted because formation of likely intermediates seems inconsistent with the low activation energy for the over-all reaction. The great similarity in activation parameters, especially $\Delta S_2^{\ddagger}$, indicates that the same mechanism is operative for all of the trifluoroacetato complexes studied thus far.

Table IV

Activation Parameters for Alkaline Hydrolysis of Trifluoroacetatopentaammine Complexes[a]

	First order		Second order		
Complex	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, eu	$\Delta H_2^{\ddagger}$, kcal mol^{-1}	$\Delta S_2^{\ddagger}$, eu	Ref
$(NH_3)_5CrO_2C_2F_3^{2+}$	...	...	6.62[b]	−34.3[b]	This work
$(NH_3)_5CoO_2C_2F_3^{2+}$	22.7	10	6.8	−37	2a
$(NH_3)_5RhO_2C_2F_3^{2+}$	18.0	−13	7.5	−36	2b

[a] All values are for ionic strength 1.0 M adjusted with NaCl.
[b] The values of k_2 calculated from these parameters at 20, 25, 30, and 35° are 2.25, 2.77, 3.39, and 4.12, respectively. These may be compared to the experimental values given in Table II.

[11] Reference 9, p 180.

Contribution from the Shell Development Company,
Emeryville, California 94608

Electrochemical Preparation of Rhodium(0) Complexes

By D. C. Olson and W. Keim

Received February 13, 1969

In recent years considerable interest has developed in coordination compounds containing metals in their lower oxidation states. These compounds are generally prepared by the chemical reduction of similar compounds containing the metal in a higher oxidation state. The use of electrochemical reduction for this purpose has not been investigated to any appreciable extent, although it should have certain advantages over chemical reduction in many applications. For example (a) since the redox chemistry of the starting materials can be examined using electrochemical techniques, it is possible to start with a better understanding of the system; (b) since the potential can be precisely controlled, a greater selectivity in reducing conditions is available; and (c) the system is probably cleaner since the reducing agent is an inert electrode. The supporting electrolytes commonly used in electrochemistry can in general be separated from the electrolysis products without undue difficulty. In many cases, where the reactants and products are sufficiently conducting, it is not necessary to add a supporting electrolyte at all.

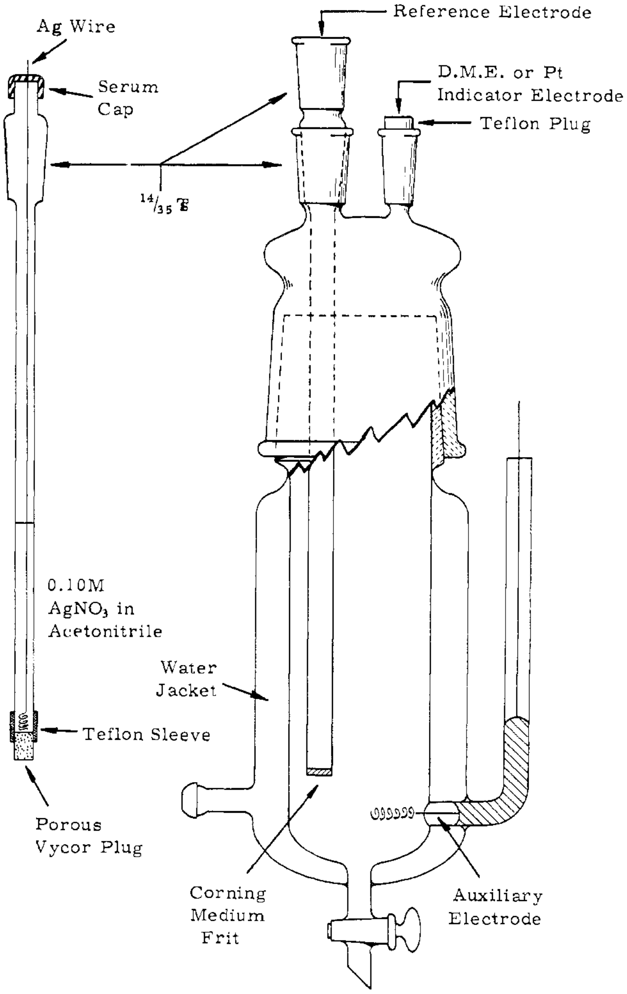


Figure 1.—Construction of the polarographic cell and reference electrode.

The preparation of two new Rh(0) complexes, $Rh((C_6H_5)_3P)_4$ and $Rh((C_6H_5)_2PCH_3)_4$, by electroreduction of Rh(I) compounds in acetonitrile is described in this paper.

Experimental Section

Apparatus.—A controlled-potential polarograph constructed in this laboratory and a Moseley 2D-2A X-Y recorder were used

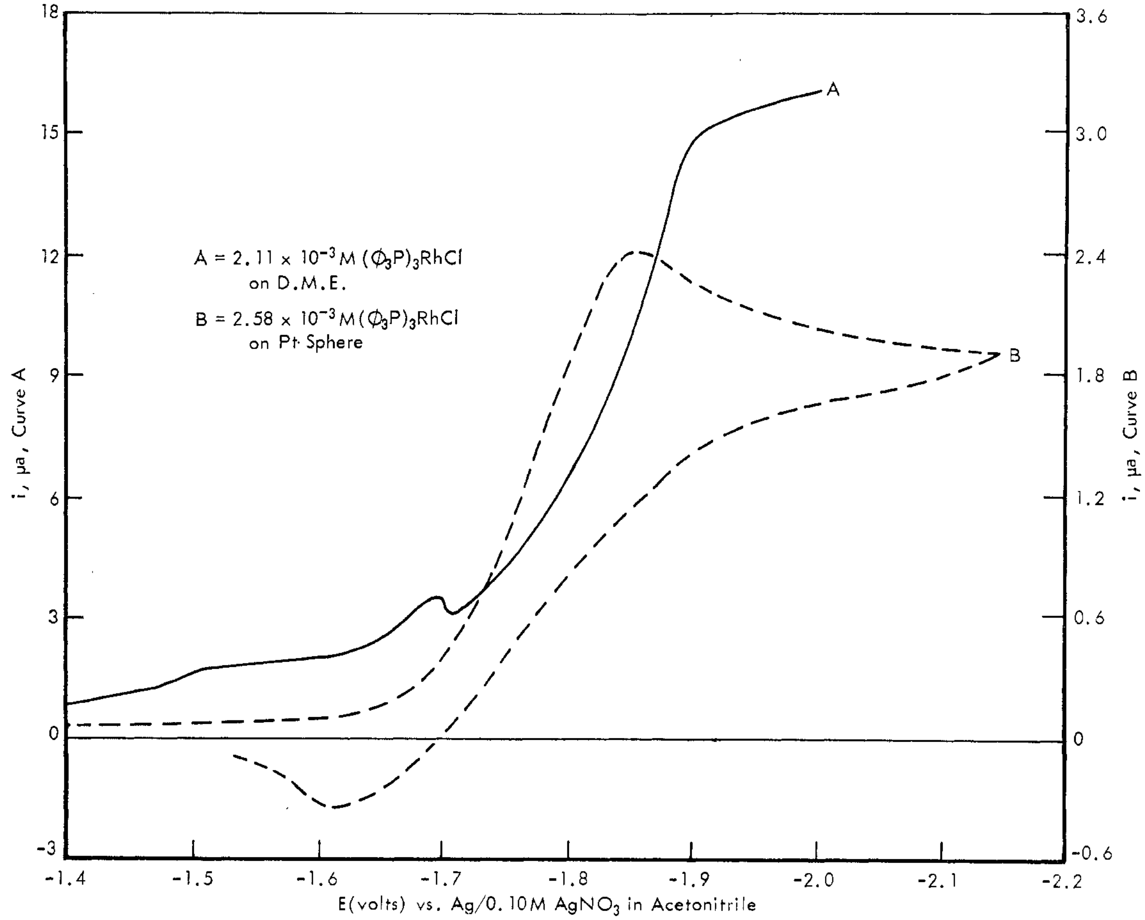


Figure 2.—Current-voltage curves of $((C_6H_5)_3P)_3RhCl$ in the presence of a 10-fold excess of $(C_6H_5)_3P$.

to obtain polarograms. The construction of the polarographic cell and the Ag–0.10 *M* $AgNO_3$ in acetonitrile reference electrode is shown in Figure 1. Both a dropping mercury electrode (dme) and a platinum sphere were used as indicator electrodes. The dme had characteristics of $m^{2/3}t^{1/6}$ of 1.49 at 0 V and 1.48 at −1.60 V. The platinum-sphere electrode, used for cyclic voltammetry, was 0.05 cm in diameter. A linear voltage sweep rate of 200 mV/min was employed with the dme and 1000 mV/min was employed with the platinum sphere. The temperature of the polarographic cell was maintained at 25.0 ± 0.1°.

A potentiostat constructed in this laboratory was employed for controlled-potential electrolysis. The cell was a 125-ml erlemeyer flask with two side arms. One of the side arms contained the reference electrode separated from the cell solution by a Corning medium frit. The other side arm contained an inner and outer compartment. The inner compartment was 2 cm in length and was separated from the cell solution by a Corning coarse frit and from the outer compartment by a Corning medium frit. The auxiliary electrode was placed in the outer compartment. This arrangement minimized mixing of the products formed at the working and auxiliary electrodes. A platinum sheet served as the working electrode.

All electrochemical work and isolation of the products were done in a Vacuum Atmospheres Dri-Lab.

Reagents.—The acetonitrile used for the electrochemical work was Mallinckrodt Nanograde purified by a procedure previously described.[1] Eastman Kodak tetraethylammonium perchlorate recrystallized five times from water and dried under vacuum at 70° was used as supporting electrolyte. The preparations of $((C_6H_5)_3P)_3RhCl$[2] and $((C_6H_5)_2PCH_3)_3RhCl$[3] have been described previously.

Electrochemical Preparation of the Rh(0) Complexes.—Electroreduction of $((C_6H_5)_3P)_3RhCl$ was carried out in 85% acetonitrile–15% toluene to enhance solubility of the complex. A solution containing 1.9 g of the complex and 4.5 g of $(C_6H_5)_3P$ in 150 ml of solvent which was 0.1 *M* in tetraethylammonium perchlorate was electrolyzed at −2.3 V to about 98% completion, as indicated by the current reading on the potentiostat. The product precipitated as a light-green solid which was filtered, washed with acetonitrile, and dried under vacuum at room temperature (yield 70%). The compound was found to decompose at 175–179°. *Anal.* Calcd for $((C_6H_5)_3P)_4Rh$: C, 74.9; H, 5.3; P, 10.8; Rh, 8.9. Found: C, 75.2; H, 5.4; P, 10.9; Rh, 8.2. The complex $((C_6H_5)_3P)_4Rh$ (1.3 g) was heated under vacuum with 3 g of phenol to 150°. The absence of hydrogen was proven by mass spectroscopy.

Electroreduction of $((C_6H_5)_2PCH_3)_3RhCl$ was carried out in acetonitrile. A solution containing 1.8 g of the complex and 7.5 g of the ligand in 200 ml of solution was electrolyzed at −2.2 V. The product precipitated as a black solid which was treated in the same manner as described above (yield 74%). *Anal.* Calcd for $((C_6H_5)_2PCH_3)_4Rh$: C, 69.2; H, 5.8; P, 13.7; Rh, 11.4. Found: C, 69.6; H, 6.1; P, 13.4; Rh, 11.6.

Results and Discussion

As shown in Figure 2 and Table I, $((C_6H_5)_3P)_3RhCl$ in the presence of a 10-fold excess of $(C_6H_5)_3P$ gave a cathodic polarographic wave with an $E_{1/2}$ of −1.833 V *vs.* an Ag–0.10 *M* $AgNO_3$ in acetonitrile reference electrode. The diffusion constant, I_d, is characteristic of a one-

---

[1] E. O. Sherman, Jr., and D. C. Olson, *Anal. Chem.*, **40**, 1174 (1968).

[2] W. Keim, *J. Organometal. Chem.* (Amsterdam), **8**, 25 (1967).

[3] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 540 (1968).

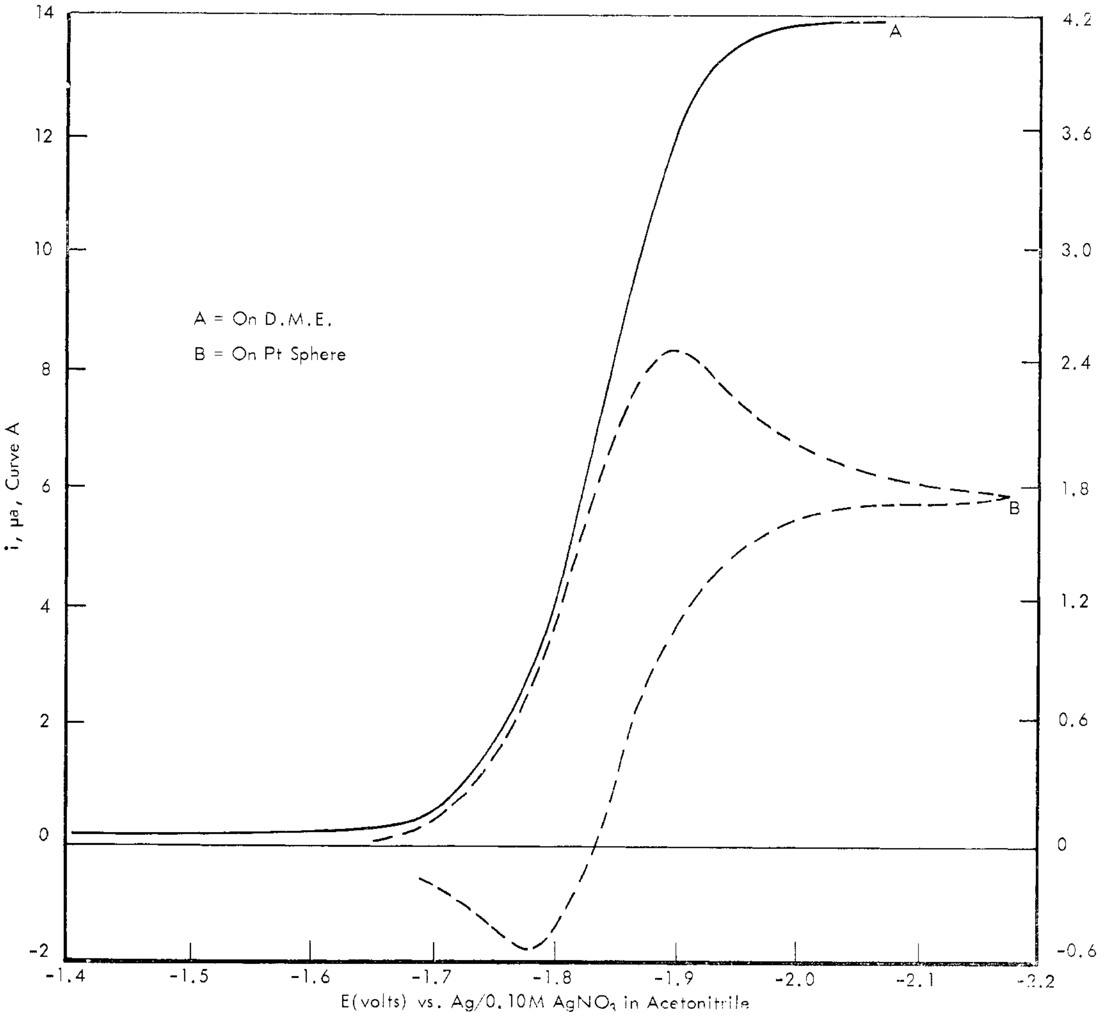


Figure 3.—Current–voltage curves of 2.00 × 10^{-3} *M* $((C_6H_5)_2CH_3P)_3RhCl$ in the presence of a 10-fold excess of $(C_6H_5)_2CH_3P$.

TABLE I

POLAROGRAPHIC PROPERTIES OF L_3RhCl IN ACETONITRILE

Complex	Concn, m*M* Complex	Concn, m*M* Ligand	$E_{1/2}$, V	Slope, mV	i_d, μA	I_d,[a]
$((C_6H_5)_3P)_3RhCl$	2.11	30.2	−1.833	99	12.3	3.11
$((C_6H_5)_2PCH_3)_3RhCl$	2.00	36.4	−1.832	84	13.6	4.65

[a] $I_d = i_d/Cm^{2/3}t^{2/6}$, where i_d is expressed in μA, *C* in mmol/l., *m* in mg/sec, and *t* in sec.

electron reduction. A cyclic voltammogram (Figure 2) exhibited an anodic peak on the reverse sweep which occurred at a potential much more negative than that expected for the dissolution of rhodium metal. This fact, together with the observation of a red color at the electrode surface during reduction, indicated that a Rh (0) complex was a product of the electrode reaction.

A polarogram and cyclic voltammogram of $((C_6H_5)_2PCH_3)_3RhCl$ in the presence of a 10-fold excess of ligand is shown in Figure 3. The electrochemical behavior of $((C_6H_5)_2PCH_3)_3RhCl$ is very similar to that of $((C_6H_5)_3P)_3RhCl$. Its polarographic $E_{1/2}$ is −1.832 V and an anodic peak was observed on the reverse sweep of the cyclic voltammogram. The I_d value obtained from the polarographic wave is larger than that expected for a one-electron reduction. However, as shown by elemental analyses of the product isolated from the electroreduction of the Rh(I) compound, the electrode reaction involves one electron.

Constant-potential electrolysis of both $((C_6H_5)_3P)_3RhCl$ and $((C_6H_5)_2PCH_3)_3RhCl$ in the presence of a 10-fold excess of ligand yielded a crystalline product insoluble in acetonitrile, but very soluble in toluene. Elemental analyses showed the products to have the stoichiometric formula RhL_4, where L is the phosphine ligand. Both samples contained a small amount of oxygen, indicating that some of the ligand might be present as the phosphine oxide. However, no infrared bands attributable to $(C_6H_5)_3PO$ were observed in the product. Purification of the $(C_6H_5)_3P$ used in the preparation of $Rh((C_6H_5)_3P)_4$ yielded a product with a lower oxygen content (<0.5%) but did not eliminate it completely. One of the reviewers suggested that a possible source of $(C_6H_5)_3PO$ is the reaction between ClO_4^- and

$(C_6H_5)_3P$,[4] in which case a pure product might be obtained if a different supporting electrolyte were used. Recent publications[5] on low-valent rhodium and iridium compounds reveal that in complexes of the above type hydrido species can be formed by abstracting a hydrogen atom from the coordinated ligand or applied solvent. The presence of a rhodium–hydrogen complex in our compounds, however, has been ruled out by ir analysis and by the reaction with phenol, which should lead to the formation of hydrogen.[5d]

Since Rh(0) has a d^9 electronic configuration, its complexes should be paramagnetic. Magnetic susceptibility measurements, however, showed that $Rh((C_6H_5)_3P)_4$ is essentially diamagnetic while $Rh((C_6H_5)_2PCH_3)_4$ is paramagnetic with a magnetic moment (1.16 BM) much less than that expected for one unpaired electron. These results can be understood by considering a metal–metal interaction similar to that found in $[Co(CO)_4]_2$

$$\underset{\text{diamagnetic}}{L_4Rh\text{–}RhL_4} \rightleftharpoons \underset{\text{paramagnetic}}{2L_4Rh}$$

---

[4] E. W. Abel, *Chem. Commun.*, 465 (1968).

[5] (a) M. A. Bennett and D. L. Milner, *ibid.*, 581 (1967); (b) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); (c) G. Hata, A. Miyake, and H. Kondo, *J. Am. Chem. Soc.*, **90**, 2278 (1968); (d) W. Keim, *J. Organometal. Chem.* (Amsterdam), **14**, 179 (1968); (e) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Commun.*, 548 (1968).

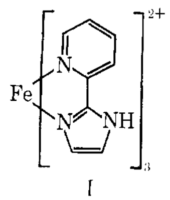
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7, ENGLAND

A New Example of $^5T_{2g}$–$^1A_{1g}$ Equilibrium for Iron(II)

BY D. M. L. GOODGAME AND A. A. S. C. MACHADO

Received April 7, 1969

There is at the present time appreciable interest in compounds of iron(II) which have a thermally accessible $^5T_{2g}$ level lying above a $^1A_{1g}$ ground state[1] and which consequently display anomalous temperature dependence of their magnetic susceptibilities.[2] We report here a new example of a species having this type of behavior, the tris-chelate cation (I) of iron(II) with 2-(2′-pyridyl)imidazole (=L)



I

The formation constants for the species FeL^{2+}, FeL_2^{2+}, and FeL_3^{2+} in aqueous solution have been determined by Eilbeck and Holmes,[3] and deep red $[FeL_3](ClO_4)_2 \cdot H_2O$ was isolated by Chiswell, *et al.*,[4] who reported it as having a magnetic moment of 5.42 BM at 293°K. As part of our research program concerning the electronic properties of metal complexes with ligands containing the imidazole ring we prepared samples of this compound but found it to have a magnetic moment of only 2.50 BM at 293°K. Variable-temperature magnetic studies showed that the magnetic moments were markedly temperature dependent. (Table I lists the results for a typical run, which involved cooling the sample from room temperature to *ca.* 86°K, heating it to *ca.* 342°K, and then cooling it to room temperature again.) The susceptibility at each temperature was independent of field strength, measurements of different samples gave reproducible results, and there was no time dependence such as that observed for $Fe(phen)_2X_2$ (X = NCS or NCSe)[5] and bis(2-(2-pyridylamino)-4-(2-pyridyl)thiazole)iron(II) nitrate.[6] Moreover, results obtained cooling the sample and those obtained at increasing temperatures fell on the same curve (Figure 1). These results indicate the presence of a spin equilibrium between a $^1A_{1g}$ ground state and a thermally accessible $^5T_{2g}$ level in this compound.

Mössbauer measurements support this conclusion. At room temperature the Mössbauer spectrum consisted of a strong doublet centered at +0.63 mm/sec[7] with a quadrupole splitting (QS) of 0.37 mm/sec. There was also a weak band at *ca.* +2.24 mm/sec and a weak shoulder at *ca.* +0.25 mm/sec on the low-velocity component of the strong doublet. At 80°K the doublet had increased in intensity (with isomer shift, $\delta = 0.71$ mm/sec and QS = 0.54 mm/sec) but the weak absorptions in the +0.25- and +2.24-mm/sec regions had virtually disappeared. These results are consistent with the presence of iron atoms in $S = 0$ and $S = 2$ states with slow relaxation (this contrasts with the Mössbauer results for iron(III) dithiocarbamates where fast electronic relaxation between the spin states results in time-averaged spectra).[8]

The strong doublet centered at +0.63 mm/sec is attributed to the iron atoms in the $S = 0$ state. The QS is larger than those reported for some other low-spin tris-chelate iron(II) cations (*e.g.*, for $Fe(phen)_3^{2+}$ QS ≈ 0.16 mm/sec[9]) presumably because the unsymmetrical nature of L as a chelate induces a greater departure from O_h symmetry with a concomitant increase in the splitting of the $^5T_{2g}$ level.

The weak band in the +2- to +2.5-mm/sec region represents one component of the $S = 2$ absorption. The other component appears as the weak shoulder at

---

[1] O_h notation is used here and subsequently for convenience, although it is recognized that the metal atom site symmetries in these and previously reported compounds of this type are lower than this.

[2] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.* (London), **22**, 457 (1968).

[3] W. J. Eilbeck and F. Holmes, *J. Chem. Soc., A*, 1777 (1967).

[4] B. Chiswell, F. Lions, and B. Morris, *Inorg. Chem.*, **3**, 110 (1964).

[5] A. T. Casey and F. Isaac, *Australian J. Chem.*, **20**, 2765 (1967).

[6] R. N. Sylva and H. A. Goodwin, *ibid.*, **20**, 479 (1967).

[7] All shifts are relative to the center of the spectrum of sodium nitroprusside at 293°K.

[8] R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966).

[9] R. R. Berrett, B. W. Fitzsimmons, and A. A. Owusu, *J. Chem. Soc., A*, 1575 (1968).