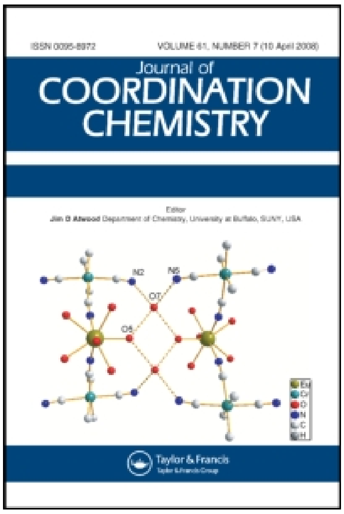

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

EQUILIBRIUM STUDIES OF THE REACTION BETWEEN TETRACHLOROPALLADIUM(II) ANION AND SULFOXIDES. THE FORMATION OF THE MONO-S-SULFOXIDE COMPLEXES

Luciano Canovese[a]; Lucio Cattalini[a]; Giampaolo Marangoni[a]; Gianni Michelon[a]; Marino Nicolini[b]; Martin L. Tobe[c]
[a] Istituto di Chimica Generale ed Inorganica, University of Venice, Italy [b] Faculty of Farmacy, University of Padova, Italy [c] William Ramsay and Ralph Forster Laboratories, University College, London, England

To cite this Article Canovese, Luciano , Cattalini, Lucio , Marangoni, Giampaolo , Michelon, Gianni , Nicolini, Marino and Tobe, Martin L.(1983) 'EQUILIBRIUM STUDIES OF THE REACTION BETWEEN TETRACHLOROPALLADIUM(II) ANION AND SULFOXIDES. THE FORMATION OF THE MONO-S-SULFOXIDE COMPLEXES', Journal of Coordination Chemistry, 12: 2, 63 — 69

To link to this Article: DOI: 10.1080/00958978308073832

URL: http://dx.doi.org/10.1080/00958978308073832

J. Coord. Chem., 1982, Vol. 12, pp. 63–69
0095-8972/82/1202-0063 $6.50/0

EQUILIBRIUM STUDIES OF THE REACTION BETWEEN TETRACHLOROPALLADIUM(II) ANION AND SULFOXIDES. THE FORMATION OF THE MONO-S-SULFOXIDE COMPLEXES

LUCIANO CANOVESE, LUCIO CATTALINI,† GIAMPAOLO MARANGONI and GIANNI MICHELON

University of Venice, Italy, Istituto di Chimica Generale ed Inorganica

MARINO NICOLINI

University of Padova, Italy, Faculty of Farmacy.

and

MARTIN L. TOBE

William Ramsay and Ralph Forster Laboratories, University College, London, England.

(*Received January 30, 1982*)

The equilibrium coefficient, K_1, for the reaction $[PdCl_4]^{2-} + RR'SO \rightleftarrows [Pd(RR'SO)Cl_3]^- + Cl^-$, has been determined for dimethylsulfoxide, tetramethylensulfoxide, and phenylmethylsulfoxide and found to be 67, 46 and 8.8 respectively at 25°C, $\mu = 1.0$ in 95:5 methanol-water. Values for the equilibrium constants for the dimethylsulfoxide complex are also reported at other ionic strengths. The equilibrium constants for the second stage, $[Pd(Me_2SO)Cl_3]^- + Me_2SO \rightleftarrows$ trans-$[Pd(Me_2SO)_2Cl_2] + Cl^-$, has been determined for dimethylsulfoxide only, $K_2 = 2.5 \times 10^{-2}$ at 25°C (μ not controlled). The causes of the mutual destabilisation of two dimethylsulfoxides are discussed.

INTRODUCTION

Sulfoxides are ambident ligands with the ability to bond through sulfur or oxygen. With the "soft" or "class b" metals such as palladium and platinum, there is a strong preference for S-bonding as indicated by solid state infrared and X-ray diffraction and solution n.m.r. studies.[1] In sterically hindered systems it is possible to find the sulfoxide bound to Pd or Pt through the oxygen. In many respects sulfoxides seem to be unusual ligands. The S-sulfoxide exerts a moderately strong *trans*-effect but is a weak nucleophile; their nucleophilicity seems to be remarkably sensitive to charge and to steric effects and mutual labilisation of two sulfoxides in the *cis* position can be considerable.[2] Since these phenomena are kinetic in origin it is of interest to see the extent to which these features also enter into equilibrium studies so as to separate ground state contributions from those of the transition state.

In this paper we report the results of a study of the reaction

$$[PdCl_4]^{2-} + RR'SO \rightleftarrows [Pd(RR'SO)Cl_3]^- + Cl^- \qquad (1)$$

---

†To whom correspondence should be addressed.

together with the second stage of the reaction with Me_2SO,

$$[Pd(Me_2SO)Cl_3]^- + Me_2SO \rightleftarrows \text{trans-}[Pd(Me_2SO)_2Cl_2] + Cl^- \tag{2}$$

EXPERIMENTAL

Reagents

K_2PdCl_4 (Engelhart) was used as obtained and the sulfoxides were purchased from Aldrich and purified before use. *Trans*-$[Pd(Me_2SO)_2Cl_2]$ was prepared according to the methods reported in the literature.[3]

Measurements

The equilibrium quotients were determined spectrophotometrically in methanol containing 5% by volume of water at 25°C. Excess chloride, added as LiCl, was used to suppress hydrolysis, prevent any significant contribution from higher sulfoxide complexes and to maintain constant ionic strength. Absorbance measurements were made with a Varian-Cary 219 double beam spectrophotometer. Preliminary studies proved that $[PdCl_4]^{2-}$/LiCl solutions obeyed Beer's law, as did the sulfoxide solutions. Solutions containing the required quantities of reagents were made up from standard solutions and allowed to reach thermal and chemical equilibrium in the spectrophotometer cell before the spectrum was measured. Accurate absorbancies were obtained at the wavelengths chosen for the subsequent analyses.

Treatment of the data

Under conditions where only two palladium species are present in significant quantities (justified in the following section) we can write the equilibrium coefficients for the reaction (1) in the form $A + R \rightleftarrows x$, as

$$K_1 = x/(A_0 - x)\,(R_0 - x) \tag{3}$$

where $A = [A_0 - x]$, $R = [R_0 - x]$, $R_0 = L_0/Y_0$, $x = [Pd(RR'SO)Cl_3^-]_{eq}$, $A_0 = [PdCl_4^{2-}]_0 = [PdCl_4^{2-}]_{eq} + [Pd(RR'SO)Cl_3^-]_{eq}$, $Y_0 = [Cl^-]_0 = [Cl^-]_{eq}$ since $[Cl^-]_0 \gg A_0$ and $L_0 = [RR'SO]_0$.

For reason of convenience we used the following expression:

$$K^* = 1/K_1 = (A_0 - x)\,(R_0 - x)/x \tag{4}$$

Solving the quadratic equation (4) gives

$$x = \tfrac{1}{2}\{(K^* + A_0 + R_0) - [(K^* + A_0 + R_0)^2 - 4A_0R_0]^{\frac{1}{2}}\} \tag{5}$$

The absorbance at the chosen wavelength, D, is given by

$$D = \varepsilon_A A_0 + x(\varepsilon_B - \varepsilon_A) \tag{6}$$

where ε_A and ε_B are the molar extinction coefficients for $[PdCl_4]^{2-}$ and $[Pd(RR'SO)Cl_3]^-$ at the chosen wavelength respectively. Using known values for ε_A (independently determined) and A_0, values of K^* and ε_B were obtained using a non-linear regression programme, which is described elsewhere,[14] with D and R_0 as variables. It must be remembered that $K_1 = 1/K^*$.

In the second stage, again under conditions where only two palladium species were present, i.e. *trans*-$[Pd(Me_2SO)_2Cl_2]$ and $[Pd(Me_2SO)Cl_3]^-$, we used the same programme with $R_0^* = Y_0^*/L_0^*$ and D as variables ($L_0^* = [Me_2SO]_0 = [Me_2SO]_{eq}$ since $L_0^* \gg A_0$, $A_0 = [\textit{trans-}Pd(Me_2SO)_2Cl_2]_0$ and $Y_0^* = [Cl^-]_0$). In this case $K_2 = 1/K'$ where K' refers to the equilibrium:

$$\text{trans-}[Pd(Me_2SO)_2Cl_2] + Cl^- \rightleftarrows [Pd(Me_2SO)Cl_3]^- + Me_2SO$$

RESULTS

The Equilibria $[PdCl_4]^{2-} + RR'SO \rightleftarrows [Pd(RR'SO)Cl_2]^- + Cl^-, K_1$

If the spectra of a series of solutions with a constant initial concentration of $[PdCl_4]^{2-}$ and a varying ratio of $R_0 = [RR'SO]_0/[Cl^-]_0$ are superimposed, many pass through an isosbestic point (at 463 nm when RR'SO = Me_2SO). Slight departures appear at higher sulfoxide and low chloride concentrations, consistent with the formation of higher sulfoxide complexes. Sufficient chloride was added to suppress solvolysis when no sulfoxide was present and the spectrum of this solution also passes through the isosbestic point. This, coupled with the fact that the absorbance change is consistent with a dependence on the first power of [RR'SO], is clear evidence that the equilibrium being studied is given by Eq. (1). Only the data from those spectra that pass exactly through the isosbestic point were used in the analyses for K_1. Equilibrium (1) will exhibit a primary salt effect and must therefore be studied at constant ionic strength. However, the concentrations of Cl^- required to prevent solvolysis on the one hand and restrict the formation of higher complexes on the other, are high enough to be in a region where secondary salt effects, resulting from the replacement of Cl^- by ClO_4^- for example, are appreciable. For this reason the ionic strength was held constant by LiCl and Y_0 could not be varied in any study. K_1 was determined at $\mu = 1.0$ for all sulfoxides and in the case of Me_2SO other sets of data at $\mu = 2.0$ and 0.514 were determined in order to see the effect of ionic strength and also to see whether ε_B was independent of μ and Y_0. Values of D at 400 nm as a function of L_0 are given in Table I and the values of K_1 and ε_B obtained from a nonlinear regression analysis are collected in Table II. In view of the criticism[5] of spectrophotometric investigations of equilibria by linear relationships such as those of Benesi and Hildebrand[6] and Brown[7] it is pleasing to note that treatment of the data in Table I by these methods gives very satisfactory agreement for K_1 and, where relevant, for ε_B as well.

The Equilibrium $[Pd(Me_2SO)Cl_3]^- + Me_2SO \rightleftarrows \textit{trans-}[Pd(Me_2SO)_2Cl_2] + Cl^-, K_2$.

In the presence of lower concentrations of chloride and the higher concentrations of sulfoxide the equilibrium associated with the addition of the second sulfoxide becomes measurable. The reaction was studied in the case of dimethylsulfoxide only. It was necessary to use conditions where $L_0^* \gg$[complex] and, in order to be able to use the same program for calculating the data it was convenient to provide the palladium complex as *trans*-$[Pd(Me_2SO)_2Cl_2]$ and to analyse the dependence of D on R_0^* in terms of K_2 for the equilibrium

$$\text{trans-}[Pd(Me_2SO)_2Cl_2] + Cl^- \rightleftarrows [Pd(Me_2SO)_3Cl^-] + Me_2SO, K'$$

Clearly, in order to obtain K' (the equilibrium constant for the addition of the second sulfoxide) it is necessary to use the relationship $K_2K' = 1$.

The charge types do not change in this equilibrium and so it is not expected to exhibit a primary salt effect. Consequently, no effort was made to maintain a constant ionic strength and LiCl was varied without any compensating addition of $LiClO_4$. The spectra of solutions of *trans*-$[Pd(Me_2SO)_2Cl_2]$ in 95:5 MeOH:H_2O were studied in the presence of varying amounts of Me_2SO and LiCl. At moderately high Me_2SO the spectra converged as $[Cl^-]$ was reduced and this was taken to be that of trans-$[Pd(Me_2SO)_2Cl_2]$. Values of ε_C were taken from this spectrum. Keeping L_0^* constant and varying Y_0^* gave a series of spectra with two

TABLE I
Measured parameters for the reaction $[PdCl_4]^{2-} + RR'SO \leftrightarrows [Pd(RR'SO)Cl_3]^- + Cl^-$

	A_0	Y_0	L_0	D
RR'SO = Me_2SO	1.07×10^{-3}	0.9925	2.99×10^{-1}	0.641
	1.07×10^{-3}	0.9925	1.02×10^{-1}	0.589
	1.07×10^{-3}	0.9925	8.12×10^{-2}	0.579
	1.07×10^{-3}	0.9925	5.10×10^{-2}	0.527
	1.07×10^{-3}	0.9925	3.00×10^{-2}	0.454
	1.07×10^{-3}	0.9925	1.00×10^{-2}	0.293
	1.07×10^{-3}	0.9925	8.00×10^{-3}	0.264
	1.07×10^{-3}	0.9925	5.00×10^{-3}	0.189
	1.07×10^{-3}	0.9925	4.00×10^{-3}	0.171
	1.07×10^{-3}	0.9925	3.00×10^{-3}	0.136
	1.07×10^{-3}	0.9925	2.00×10^{-3}	0.117
RR'SO = $(CH_2)_4SO$	1.05×10^{-3}	0.999	3.62×10^{-1}	0.766
	1.05×10^{-3}	0.999	1.81×10^{-1}	0.724
	1.05×10^{-3}	0.999	1.00×10^{-1}	0.682
	1.07×10^{-3}	0.993	8.00×10^{-2}	0.655
	1.07×10^{-3}	0.993	5.00×10^{-2}	0.580
	1.07×10^{-3}	0.993	3.00×10^{-2}	0.487
	1.07×10^{-3}	0.993	1.00×10^{-2}	0.283
	1.07×10^{-3}	0.993	8.00×10^{-3}	0.247
	1.07×10^{-3}	0.993	5.00×10^{-3}	0.186
	1.07×10^{-3}	0.993	4.00×10^{-3}	0.159
	1.07×10^{-3}	0.993	3.00×10^{-3}	0.132
	1.07×10^{-3}	0.993	2.00×10^{-3}	0.103
RR'SO = Ph(Me)SO	1.05×10^{-3}	0.999	1.297	0.808
	1.05×10^{-3}	0.999	1.037	0.795
	1.05×10^{-3}	0.999	7.78×10^{-1}	0.771
	1.05×10^{-3}	0.999	6.62×10^{-1}	0.751
	1.05×10^{-3}	0.999	3.89×10^{-1}	0.680
	1.05×10^{-3}	0.999	1.94×10^{-1}	0.536
	1.07×10^{-3}	0.993	1.00×10^{-1}	0.449
	1.07×10^{-3}	0.993	8.00×10^{-2}	0.395
	1.07×10^{-3}	0.993	5.00×10^{-2}	0.293
	1.07×10^{-3}	0.993	3.00×10^{-2}	0.208
	1.07×10^{-3}	0.993	1.00×10^{-2}	0.105
	1.07×10^{-3}	0.993	8.00×10^{-3}	0.092
	1.07×10^{-3}	0.993	5.00×10^{-3}	0.070
	1.07×10^{-3}	0.993	4.00×10^{-3}	0.065
	1.07×10^{-3}	0.993	3.00×10^{-3}	0.057
	1.07×10^{-3}	0.993	2.00×10^{-3}	0.055

TABLE II
Measured values for the extinction coefficients and the equilibrium constants for the reactions $[PdCl_4^{2-}] + RR'SO \rightleftarrows [Pd(RR'SO)Cl_3^-] + Cl^-$ at 400 nm

RR'SO	ε_A	ε_B	K_1
Me_2SO	40 ± 2	628 ± 6	67 ± 2
$(CH_2)_4SO$	40 ± 2	765 ± 3	46.0 ± 0.5
Ph(Me)SO	40 ± 2	827 ± 7	8.8 ± 0.3

TABLE III

Measured parameters for the reaction trans-$[Pd(Me_2SO)_2Cl_2] + Cl^- \rightleftarrows [Pd(Me_2SO)Cl_3]^- + Me_2SO$ and measured values for the extinction coefficients and the equilibrium constant, at 400 and 380 nm

A_0	$R_0^* = Y_0^*/L_0^*$	D_{400}	D_{380}
7.7×10^{-4}	5.0×10^{-1}	0.495	0.518
	4.0×10^{-1}	0.495	0.521
	2.5×10^{-1}	0.500	0.525
	1.5×10^{-1}	0.505	0.530
	5.0×10^{-2}	0.530	0.571
	4.0×10^{-2}	0.539	0.582
	2.5×10^{-2}	0.562	0.613
	1.5×10^{-2}	0.575	0.638
	7.5×10^{-3}	0.601	0.673
	5.0×10^{-3}	0.614	0.691
	2.5×10^{-3}	0.630	0.711
400 nm:	$\varepsilon_C = 822 \pm 4$	$\varepsilon_B = 630 \pm 4$	$K' = 40 \pm 3$
380 nm:	$\varepsilon_C = 930 \pm 3$	$\varepsilon_B = 655 \pm 6$	$K' = 39 \pm 3$

isosbestic points. At very low value of Y_0^* these isosbestic points were lost as a result of solvolysis. Data for the subsequent analysis were only taken from those spectra that passed through the isosbestic points. As [LiCl] is increased the spectra converge at the same final spectrum as found on the $PdCl_4^{2-} + Me_2SO$ study.

The data for the dependence of D on R_0^* is given in Table III. In this case data at 380 and 400 nm were used. Both give the same values for K′, 39 ± 3 and 40 ± 3, and it is important to note that the value of ε_B at 400 nm determined in this way, 630 ± 4 m.mol.cm^{-2}, agrees very well with that determined starting from $PdCl_4^{2-}$, 628 ± 6 m.mol.cm^{-2}. This is further evidence that the second equilibrium is indeed being studied in these experiments.

DISCUSSION

At constant ionic strength ($\mu = 1.0$) the equilibrium coefficients for reaction (1) decrease along the sequence, dimethylsulfoxide (65) > tetramethylenesulfoxide (46) > phenylmethylsulfoxide (8.4). If the difference in complex forming ability was due to changes in the σ-donor ability of sulfur, resulting from the changing inductive effects of the substituents, it would have been predicted that tetramethylenesulfoxide ($-\Sigma\sigma^* = 0.18$[8]) > dimethylsulfoxide ($-\Sigma\sigma^* = 0$) > phenylmethylsulfoxide ($-\Sigma\sigma^* = -0.6$), and so the inversion of results for the first two sulfoxides is slightly surprising. Steric hindrance, which is thought to be important in the behaviour of sulfoxides,[1] might have accounted for the lower value of the phenylmethylsulfoxide but there is little difference between Me_2SO and $(CH_2)_4SO$; if anything the latter offers less hindrance. Steric effects therefore predict the same sequence as inductive effects. It is possible that the relatively small differences arise from the change in the π-electron density on the sulfur, with hyperconjugation from the methyl group as a major factor. However, it is rash to place too much emphasis on electronic effects when the differences are so small.

The most significant observation in this work is the very large difference between the first and second "successive stability constants" (bearing in mind that chloride, and not solvent, is being displaced by the sulfoxide), $\log K_1 = 1.81$; $\log K_2 = -1.60$. A purely statistical model would predict much smaller differences and the charge effects would narrow the gap still further. For example, the equilibrium coefficients for the solvolysis of $[PdCl_4]^{2-}$, $[PdCl_4]^{2-} + H_2O \rightleftarrows [PdCl_3(H_2O)]^- + Cl^-$, $\log K_1 = -2.6$; $[PdCl_3(H_2O)]^- + H_2O \leftrightarrows [PdCl_2(H_2O)_2] + Cl^-$, $\log K_2 = -2.5$[9] are almost identical and the reactions are of the same charge type as those under discussion. Until now, quantitative studies of the unusual coordinating properties of sulfoxides were all kinetic in nature and there is always a temptation to use the transition state as a means of explaining effects that are not manifest in the ground state. These equilibrium studies indicate that the mutual destabilisation of two sulfoxides is also present in the ground state. As already pointed out by Elding[10] there are many similarities between ethene and dimethylsulfoxide in reactions involving them and Pt or Pd. A moderately strong *trans*-effect for dmso[11] accompanied by a negligible *trans*-influence[12] is associated with a poor nucleophilicity.[9] The equilibrium coefficients for the reaction, $[PtCl_4^{2-}]$ + olefin $\rightleftharpoons$ $[Pt(olefin)Cl_3^-] + Cl^-$ in water was determined many years ago[13] but, as in the case of the platinum sulfoxide complexes, there was no indication of the binding of a second olefin. (The analogous Pd(II) reactions are complicated by subsequent reactions of the olefin). *Trans*-bis-(olefin) complexes of Pt(II) have not been yet reported and the formation of the *cis*-bis-(olefin) complexes generally requires a chelating diolefin. All of this would suggest that the difference between the first and second equilibrium coefficients for the displacement of chloride from $PtCl_4^{2-}$ (and by analogy, those for the corresponding Pd(II) reactions) is at least as marked as in the case of displacement of chloride from $PdCl_4^{2-}$ by Me_2SO. The behaviour of the olefins is generally rationalized in terms of the importance of π-bonding in their interactions with the d^8 metal ions. The bis-(dimethylsulfoxide)dichloropalladium(II) complex is known to be *trans* in the solid state[14] and there is no evidence to suggest that it isomerizes in aqueous solution. In any case, if the *cis* isomer was more stable than the *trans* and the second equilibrium coefficient referred to the formation of the *cis*-bis complex, then the effect would be further intensified since the formation coefficient for the *trans* isomer would have to be even smaller than that reported.

It is well known that sulfoxide complexes are sensitive to steric hindrance. The $[Pd(Me_2SO)_4]^{2+}$ cation has two S-bonded and two O-bonded sulfoxides because of the strain,[15] the stable $[Pt(RR'SO)_2Cl_2]$ isomers are cis and when R and R' are not bulky but *trans* when it is (e.g. R = R' = isopropyl).[15] However, in spite of the large amount of structural data now available, there is little evidence for any ground state π-bonding or of a measurable trans influence. With the exceptions of the case mentioned above the Pt (or Pd) is always bound directly to the sulfur atom and there is no evidence for sideways interaction with the S=O bond. The M—S=O bond angle is not far from tetrahedral[12,16–21] ruling out the possibility of interaction of the π^* orbital of the S=O bond (as in M—C=O complexes). The mutual labilisation of *cis* sulfoxides is not matched by any indication of ground-state repulsion[17] and there are no indications of unusually close non-bonding interactions or distorted angles at the metal in the *cis*-$[Pt(Me_2SO)_2Cl_2]$, although the Pt-S distances in this complex (2.244 and 2.229 Å) are somewhat larger than that observed in the $[Pt(Me_2SO)Cl_3]^-$ anion (2.193 Å)[11]. This, however, may be a charge effect since the Pt-S distances in other neutral mono sulfoxide complexes of the type *trans*-$[Pt(R_2SO)(am)Cl_2]$ are all in the region (2.22 to 2.23 Å).[18,19] The unusually long PtS bonds in *cis*-$[Pt(Me_2SO)_2(C_6H_5)_2]$(2.315 and 2.324 Å) are probably due to the *trans*-influence of the phenyl groups.

In summary, there is no doubt that when more than one sulfoxide is present in a Pt(II) or Pd(II) complex there is a mutual destabilisation and labilisation. Although this effect is clearly manifest in the equilibria, there is no structural evidence that clearly points to any steric or π-bonding ground state effect.

ACKNOWLEDGEMENTS

We thank the Italian Council for Research (C.N.R.-Rome) and the British Council for financial support on a bilateral research project. We also thank Mrs. L. Gemelli for technical assistance.

REFERENCES

1. F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publishers Ltd., England (1973), p. 185 and references therein.
2. M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, **20**, 1493 (1981).
3. B. B. Wayland, J. H. Price and A. N. Williamson, *Inorg. Chem.*, **11**, 1280 (1972).
4. W. E. Wentworth, W. Hirsch and E. Chen, *J. Phys. Chem.*, **71**, 218 (1967).
5. D. A. Deranlau, *J. Am. Chem. Soc.*, **91**, 4044 (1969) and references therein.
6. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
7. K. L. Brown, *Inorg. Chim Acta*, **37**, L513 (1979).
8. R. W. Taft Jr., *Steric Effects in Organic Chemistry* (M. S. Newmann Ed.), J. Wiley and Sons Inc., New York, (1956) and H. K. Hall Jr., *J. Am. Chem. Soc.* **79**, 5442 (1957).
9. H. A. Droll, B. P. Block and W. C. Fernelius, *J. Phys. Chem.*, **61**, 1000 (1957).
10. L. G. Elding and A. B. Groning, *Inorg. Chim. Acta*, **38**, 59 (1980).
11. R. Romeo and M. L. Tobe, *Inorg. Chem.*, **13**, 1991 (1974).
12. R. Melanson, J. Hubert and F. D. Rochon, *Acta Cryst.*, **B22**, 1914 (1976).
13. I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).
14. M. J. Bennet, F. A. Cotton, D. L. Weaver, R. J. Williams and W. H. Watson, *Acta Cryst.*, **23**, 788 (1967).
15. F. R. Hartley, *Chem. Rev.* 799 (1969).
16. D. A. Langs, C. R. Hare and R. G. Little, *Chem. Comm.* 1080 (1967).
17. R. Melanson and F. D. Rochon, *Can. J. Chem.*, **53**, 2371 (1975).
18. C. J. L. Lock and R. A. Speranzini, *Can. J. Chem.* **54**, 53 (1976).
19. R. Melanson and F. D. Rochon, *Inorg. Chem.*, **17**, 679 (1978).
20. R. Bardi, A. Del Pra, A. M. Piazzesi and M. Trozzi, *Cryst. Str. Comm.*, **10**, 301 (1981).
21. L. Cattalini, G. Michelon, G. Marangoni and G. Pellizzi, *J. Chem. Soc. Dalton Trans.*, 96 (1979).