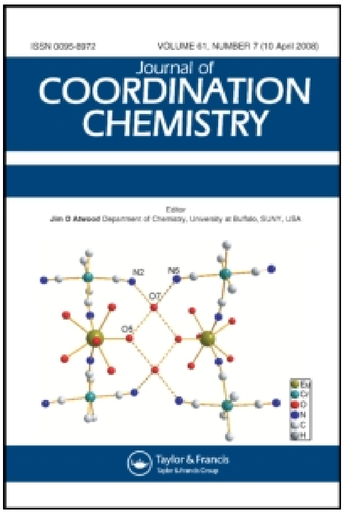

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Comparison of the Electronic Structures of Ruthenium Thionitrosyl and Ruthenium Nitrosyl Complexes: A Molecular Orbital Study

K. K. Pandey[a]
[a] School of Chemistry, Devi Ahilya University Indore, Indore, India

To cite this Article Pandey, K. K.(1990) 'Comparison of the Electronic Structures of Ruthenium Thionitrosyl and Ruthenium Nitrosyl Complexes: A Molecular Orbital Study', Journal of Coordination Chemistry, 22: 4, 307 — 313

To link to this Article: DOI: 10.1080/00958979009408229

URL: http://dx.doi.org/10.1080/00958979009408229

J. Coord. Chem. 1991, Vol. 22. pp. 307-313
Reprints available directly from the publisher
Photocopying permitted by license only

COMPARISON OF THE ELECTRONIC STRUCTURES OF RUTHENIUM THIONITROSYL AND RUTHENIUM NITROSYL COMPLEXES: A MOLECULAR ORBITAL STUDY

K. K. PANDEY

School of Chemistry, Devi Ahilya University Indore, Khandwa Road, Indore 452 001, India

(Received August 8, 1990; in final form September 26, 1990)

CNDO/2 molecular orbital calculations have been performed on the systems $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$ (X = S or O) in order to investigate the nature and energetics of the interaction between ruthenium and isoelectronic NS and NO ligands. The computed trends for Ru-N, NS and NO bond strengths in the complexes, as measured by Wiberg indices, charge distributions and orbital populations, suggest that the strength of the Ru-NS bond is greater than that of the Ru-NO bond and the NS ligand is a better electron remover from the central ruthenium atom than the NO ligand. The strength of an Ru-L (L = Cl or H_2O) bond *trans* to a NS ligand is weaker than a Ru-L bond *trans* to a NO ligand. The ratio of σ-donor to π-acceptor abilities of NS is greater than that of NO. For $[Ru(NX)Cl_5]^{2-}$, the strength of the *trans*-Ru-Cl bond is greater than that of the *cis*-Ru-Cl bond for nitrosyl complexes but the reverse is true for thionitrosyl complexes. The calculations confirm the experimental observations that the ligand positioned *trans* to an NS ligand is more labile and, hence, more susceptible to replacement than the ligand positioned *trans* to a NO ligand.

Keywords: Ruthenium, thionitrosyl, nitrosyl, complexes, molecular orbital studies

INTRODUCTION

In the recent past, considerable progress has been made in the synthesis and structural determination of transition metal thionitrosyl complexes.[1-9] A number of thionitrosyl complexes have been structurally characterized,[10-20] but little is known about their electronic structure.[21-24] In view of the resemblance between the ligands NS and NO, comparative studies on the coordinated thionitrosyl and nitrosyl ligands are of special interest. In this paper the electronic structures of $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$ (X = S or O) have been investigated by CNDO/2 molecular orbital calculations

COMPUTATIONAL DETAILS

Molecular orbital calculations were carried out using a CNDO/2-U method.[25] The orbitals 5s, 5p and 4d of ruthenium were included in the calculations. Wave functions for these orbitals were those given by Burns.[26] The wave functions for S (3s and 3p), Cl (3s and 3p), O (2s and 2p), N (2s and 2p) and H (1s) were Slater type orbitals. The values for the orbital exponent, beta and electronegativities[27] are listed in Table I.

TABLE I
Parameters used in CNDO/2 Calculations.

Atom		Orbital exponent	Beta	Mulliken's Electronegat.	Subshell Mulliken's Electronegat.
Ru	5s	1.260	−8.990	1.42	2.8545
	5p	1.260	−8.990	1.42	0.6760
	4d	2.612	−13.860	1.42	3.6264
Cl	3s	2.033	−22.330	3.160	21.5910
	3p	2.033	−22.330	3.160	8.7080
S	3s	1.817	−18.150	2.58	17.6500
	3p	1.817	−18.150	2.58	6.9890
O	2s	2.275	−31.000	3.44	25.3902
	2p	2.275	−31.000	3.44	9.1110
N	2s	1.950	−25.000	3.04	19.3160
	2p	1.950	−25.000	3.04	7.2750
H	1s	1.200	−9.000	2.20	7.1761

Atomic charges and overlap populations were obtained by a Mulliken population analysis.[28] The coordinate system adopted for $[Ru(NX)Cl_4L]^{n-}$ (X = S or O; L = Cl or H_2O) is given in Figure 1.

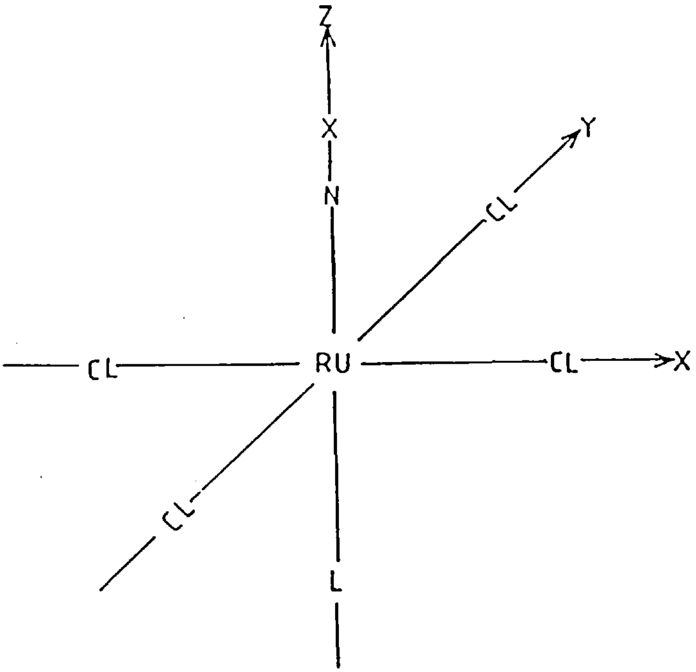

FIGURE 1 Coordinate system for $[Ru(NX)Cl_4L]^{n-}$; z axis is out of the plane.

Interatomic distances were taken from X-ray diffraction measurements when available, or otherwise estimated. In spite of the deviation from 180° reported for the angle Ru–N–X,[14,29,30] this was disregarded in the present calculations and Ru–N–X linearity was maintained. Distances in $[Ru(NS)Cl_5]^{2-}$ were estimated and they are Ru–NS 1.777 Å, *trans*-Ru–Cl 2.386 Å, *cis*-Ru–Cl 2.373 Å, and N–S 1.502 Å. Interatomic distances available in the literature for $[Ru(NO)Cl_5]^{2-}$ were used.[29] These are Ru–NO 1.738 Å, *trans*-Ru–Cl 2.357 Å, *cis*-Ru–Cl 2.376 Å, and N–O 1.131 Å. Distances reported for $[Ru(NS)Cl_4(H_2O)]^-$ were used: Ru–NS 1.729 Å, Ru–O 2.112 Å, Ru–Cl 2.376 Å, N–S 1.504 Å and O–H 0.95 Å. Distances used for $[Ru(NO)Cl_4(H_2O)]^-$ are[30] Ru–NO 1.656 Å, Ru–O 2.061 Å, Ru–Cl 2.375 Å, N–O 1.165 Å and O–H 0.95 Å. All computations were performed using the QCPE 474 Program[31] implemented on an ICIM-6000 computer.

RESULTS AND DISCUSSION

Wiberg Indices

Bond strength results (as measured by Wiberg indices[32]) are summarized in Table II. The NO and NS ligands act as σ-donors by donating electrons to the metal and also as π-acceptors by accepting electrons from the metal. The values of the Ru–N Wiberg indices ($W_{Ru-NO} < W_{Ru-NS}$) suggest that the NS ligand is a better σ-donor and π-acceptor than the NO ligand; σ-donation tends to raise the W_{N-X} index since electrons are removed from antibonding σ-orbital while π-backbonding tends to decrease W_{N-X} because the electrons enter into the antibonding π^* orbital. The increasing values of W_{N-X} in ruthenium nitrosyl complexes over ruthenium thionitrosyl complexes confirm the superior σ-donor and π-acceptor abilities of the NS ligand.

TABLE II
Bond strengths (Wiberg indices) for $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$.

Bond	$[Ru(NS)Cl_5]^{2-}$	$[Ru(NO)Cl_5]^{2-}$	$[Ru(NS)Cl_4(H_2O)]^-$	$[Ru(NO)Cl_4(H_2O)]^-$
Ru–N	1.9367	1.7874	1.8798	1.8192
σ	0.5651	0.5131	0.6075	0.5561
π	1.3716	1.2743	1.2723	1.2631
N–X	1.5323	1.6754	1.6257	1.6741
trans-Ru–Cl	0.7450	0.7606		
σ	0.6604	0.6722		
π	0.0846	0.0884		
cis-Ru–Cl	0.7517	0.7421	0.8073	0.8114
σ	0.6844	0.6753	0.7205	0.7258
π	0.0673	0.0668	0.0868	0.0856
trans-Ru–O			0.2987	0.3219
σ			0.2762	0.2963
π			0.0225	0.0256

For $[Ru(NO)Cl_5]^{2-}$, the largest difference between the components of the *cis*- and *trans*-Ru–Cl bonds occurs with the Ru(p)–Cl components (*cis*-Ru(p)–Cl = 0.3584, *trans*-Ru(p)–Cl = 0.3922). The Ru(s)–Cl (*cis*-Ru(s)–Cl = 0.1295, *trans*-Ru(s)–Cl = 0.1236) and Ru(d)–Cl (*cis*-Ru(d)–Cl = 0.2542, *trans*-Ru(d)–Cl = 0.2448) fractional bond indices are both larger for the *cis* bond but the differences are not as great as that between the aforementioned Ru(p)–Cl components which favour the *trans* bond. Similar trends for Ru(s)–Cl, Ru(p)–Cl and Ru(d)–Cl (*cis*-Ru(s)–Cl = 0.1291, *trans*-Ru(s)–Cl = 0.1230; *cis*-Ru(p)–Cl = 0.3577, *trans*-Ru(p)–Cl = 0.3830; *cis*-Ru(d)–Cl = 0.2649, *trans*-Ru(d)–Cl = 0.2390) have been found in $[Ru(NS)Cl_5]^{2-}$, but in this case the sum of the differences of Ru(s)–Cl and Ru(d)–Cl fractional bond indices is greater than the difference of Ru(p)–Cl components and hence favour the *cis* bond.

For $[Ru(NX)Cl_4L]^{n-}$ (L = Cl or H_2O), the change in σ-bonding and π-bonding due to the introduction of an Ru–NS bond with relatively large σ-bond and π-bond components result in a decrease in the *trans*-Ru–L σ-bond and an increase in the *trans*-Ru–L π-bond components. The differences in *trans*-Ru–L π-bonds are not as great as those between *trans*-Ru–L σ-bonds and the *trans*-Ru–L bonds weakened for thionitrosyl complexes. The calculations confirm the experimental observations that the chlorine atom positioned *trans* to an NS ligand is more labile and hence more susceptible to replacement than the chlorine atom positioned *trans* to an NO ligand. In the case of hydrolysis of $[Ru(NO)Cl_5]^{2-}$, the substitution requires temperatures of 50°C,[33–35] while in the case of $[Ru(NS)Cl_5]^{2-}$ substitution occurs immediately at room temperature and *trans* to the NS group.

In order to see in more detail how the substitution of an NS ligand for an NO ligand affects the bonding patterns, it is necessary to examine the various contributions to the Ru–N, *trans*-Ru–L (L = Cl or H_2O) and *cis*-Ru–Cl bond orders for $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^{-}$. Several things are apparent from these contributions; (i): the interactions of Ru($5p\pi$ and $4d\pi$) with N($2p\pi$) contribute more to the Ru–N bond order than the interactions of Ru($5s_\sigma$, $5p_\sigma$ and $4d_\sigma$) and N(s_σ and p_σ) atomic orbitals; (ii): the Ru–N σ overlap varies between 40% to 48% of the Ru–N π value; (iii): the NS ligand is a better electron acceptor and electron donor than the NO ligand; (iv): the π-acceptor to σ-donor ratio of Ru–NO is greater than that of Ru–NS; (v): although the Ru–NX overlap is always less than the Ru–Cl overlap, it is never less than 75% of the Ru–Cl value; (vi): the main contributions to the *trans*-Ru–L and *cis*-Ru–Cl bond orders are from the interactions of Ru($5s_\sigma$, $5p_\sigma$ and $4d_\sigma$) with ligand (s_σ and p_σ) atomic orbitals; (vii): the Ru–Cl π overlap is never more than 13% of the Ru–Cl σ-value; (viii): the ligand *trans* to an NO group is a better σ-donor and π-acceptor than that *trans* to an NS group.

Charge Distribution

Orbital Charges and gross atomic charges are presented in Table III. Comparison of charges on ruthenium in [RuNS] and [RuNO] complexes shows that the charges on the ruthenium in [RuNS] complexes are more positive. The larger positive charges on ruthenium in the thionitrosyl complexes suggest that the NS ligand is better electron remover from the central ruthenium atom. On substituting H_2O for Cl in the *trans* position, the charge on ruthenium decreases and that on NX increases for both thionitrosyl and nitrosyl complexes. The trend in NX charges is the same as the trend of N–X Wiberg indices and the reverse of the Ru–N Wiberg indices. Thus the NX charges are correlated with traditional π-backbonding concepts. The results of these calculations show that for $[Ru(NO)Cl_5]^{2-}$, the *cis*-Cl is a better electron acceptor from the central ruthenium atom than the *trans*-Cl, while the reverse is true for $[Ru(NS)Cl_5]^{2-}$. For $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$, the ligand *trans* to an NS group is a better electron acceptor than the ligand *trans* to an NO group.

Orbital Populations

For $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$, upon substituting an NS ligand for an NO ligand, there is an increase in the N 2pπ and X pπ populations and a decrease in the Ru 4dπ population (Table III). For nitrogen, the lowest positive charge and larger 2pπ population in the ruthenium thionitrosyl complexes are indicative of greater π-backbonding in these complexes.

TABLE III
Orbital charges and gross atomic charges for $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$ (X = S or O).

Complex	Orbital charges			Atomic charges
$[Ru(NS)Cl_5]^{2-}$	Ru	N	S	Ru = 0.6289
	5s 0.4816	2s 1.4733	3s 1.8193	N = 0.0250
	5p 1.3658	2p 3.5017	3p 4.3599	S = −0.1792
	4d 5.5237			*trans*-Cl = −0.4961
	trans-Cl	*cis*-Cl		*cis*-Cl = −0.4948
	3s 1.8579	3s 1.8582		
	3p 5.6382	3p 5.6366		
$[Ru(NO)Cl_5]^{2-}$	Ru	N	O	Ru = 0.5407
	5s 0.4800	2s 1.5065	2s 1.7481	N = 0.1898
	5p 1.3631	2p 3.3037	2p 4.4743	O = −0.2224
	4d 5.6162			*trans*-Cl = −0.4873
	trans-Cl	*cis*-Cl		*cis*-Cl = −0.5052
	3s 1.8523	3s 1.8583		
	3p 5.6350	3p 5.6469		
$[Ru(NS)Cl_4(H_2O)]^-$	Ru	N	S	Ru = 0.5802
	5s 0.4752	2s 1.4655	3s 1.8181	N = 0.0724
	5p 1.3137	2p 3.4621	3p 4.2200	S = −0.0381
	4d 5.6309			O = −0.2188
	O	Cl		Cl = −0.4485
	2s 1.5557	3s 1.8516		H = 0.1986
	2p 4.6631	3p 5.5969		
$[Ru(NO)Cl_4(H_2O)]^-$	Ru	N	O(NO)	Ru = 0.5276
	5s 0.4753	2s 1.5054	2s 1.7625	N = 0.2426
	5p 1.3164	2p 3.2520	2p 4.4250	O(NO) = −0.1875
	4d 5.6807			$O(H_2O)$ = 0.2096
	$O(H_2O)$	Cl		Cl = −0.4439
	2s 1.5483	3s 1.8505		H = 0.2010
	2p 4.6613	3p 5.5934		

The Trans *Influence*

The *trans* effect in complexes containing CO, CS, NO or NS is usually discussed in terms of competition for σ- and π-electron density by groups *trans* to each other. A simple bonding model consisting with these observations is that a ligand (like NO), with greater π/σ ratio, increases the potential for bonding of the metal σ-orbital *trans* to it and shows strengthening of the bond. A ligand (like NS), with a lower π/σ ratio, reduces the potential for bonding of metal σ-orbital *trans* to it and shows a weakening of the bond. The shortening of the bond *trans* to NO and the lengthening of the bond *trans* to NS has been observed by X-ray diffraction studies of various nitrosyl and thionitrosyl complexes (Table IV).[12-14,36-44]

TABLE IV
Effects of NX (X = S or O) on *trans*- and *cis*-metal-ligand distances (Å) in metal nitrosyl and metal thionitrosyl complexes.

Complex	*Trans*-M–X distance	*Cis*-M–X distance	*Cis-Trans*	Ref.
Nitrosyl complexes				
$Na_2[Fe(NO)(CN)_5]$	1.918(6)	1.932(3)[a]	0.014	36
$(NH_4)_2[Ru(NO)Cl_5]$	2.357(1)	2.376(1)[a]	0.019	29
$K_2[Ru(NO)Cl_5]$	2.359(2)	2.372(8)[a]	0.013	37
$Ru(NO)Cl_3(PPh_3)_2$	2.355(2)	2.394(2)[b]	0.041	38
$Ru(NO)Cl_3(PMePh_2)_2$	2.357(2)	2.398(7)[b]	0.041	39
Trans-$[Ru(NO)(NH_3)_4(OH)]Cl_2$	1.961(3)	1.99–2.10[c]	0.039	40
$[Ru(NO)(NH_3)_5]Cl_3$	2.017(1)	2.097(8)[a]	0.080	40
Trans-$Na_2[Ru(NO)(NO_2)_4(OH)]$	1.950(5)	1.99–2.10[c]	0.050	41
$K[Ir(NO)Br_5]$	2.419(4)	2.480(3)	0.061	42
$K[Ir(NO)Cl_5]$	2.286(3)	2.338(2)	0.052	43
$Os(NO)Cl_3(SnCl_3)_2$	2.364(4)	2.380(4)	0.016	44
Thionitrosyl complexes				
$Os(NS)Cl_3(PPh_3)_2$	2.399(3)	2.387(3)[b]	−0.012	12
$(PPh_4)[Ru(NS)Cl_4(H_2O)]$	2.112(3)	1.99–2.10[c]	−0.112	14
$(PPh_4)[Os(NS)Cl_4(H_2O)]$	2.178(2)	2.00–2.10[d]	−0.173	13

[a] Average of four *cis* values. [b] Average of two *cis* values. [c] Calculated from the covalent radius of Ru(II) and O. [d] Calculated from the covalent radius of Os(II) and O.

ACKNOWLEDGEMENTS

Support of this investigation by the University Grants Commission, New Delhi, is gratefully acknowledged.

REFERENCES

1. K.K.Pandey, D.K.M. Raju, U.C. Agarwala and H.L. Nigam, *Proc. Indian Natn. Sci. Acad.*, 48A, 16 (1982).
2. H.W. Roesky and K.K. Pandey, *Adv. Inorg. Radiochem.*, 26, 337 (1983).
3. P.F. Kelly and J.D. Woollins, *Polyhedron*, 5, 607 (1986).
4. T. Chivers and F. Edelmann, *Polyhedron*, 5, 1661 (1986).

K.K. Pandey, *Inorg. Chim. Acta*, **111**, 9 (1986).
U. Abram, R. Kirmse, K. Kohler, B. Lorenz and L. Kaden, *Inorg. Chim. Acta*, **129**, 15 (1987).
B.F.G. Johnson, B.L. Haymore and J.R. Dilworth, "Comprehensive Coordination Chemistry", Editor-in-Chief: G. Wilkinson, (Pergamon Press, Oxford, 1987), **2**, 118.
W.P. Griffith, "Comprehensive Coordination Chemistry", Editor-in-Chief: G. Wilkinson, (Pergamon Press, Oxford, 1987), **4**, 552.
F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5th Edn., (John Wiley and Sons, New York, 1988), 342.
T.J. Greenhough, B.W.S. Kolthammer, I. Legzdins and J. Trotter, *Inorg. Chem.*, **18**, 3548 (1979).
M.B. Hursthouse and M.J. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1362 (1979).
H.W. Roesky, K.K. Pandey, W. Clegg, M. Noltemeyer and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 709 (1984).
K.K. Pandey, H.W. Roesky, M. Noltemeyer and G.M. Sheldrick, *Z. Naturforsch.*, **39b**, 590 (1984).
J.W. Bats, K.K. Pandey and H.W. Roesky, *J. Chem. Soc., Dalton Trans.*, 2081 (1984).
R. Weber, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **504**, 13 (1983).
J. Baldas, J. Bonnyman, M.F. Mackay and G.A. Williams, *Aust. J. Chem.*, **37**, 751 (1984).
J. Anhaus, Z.A. Siddigi, H.W. Roesky, J.W. Bats and Y. Elerman, *Z. Naturforsch.*, **40b**, 740 (1985).
W. Willing, U. Müller, U. Demant and K. Dehnicke, *Z. Naturforsch.*, **41b**, 560 (1986).
U. Demant, W. Willing, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **532**, 175 (1986).
H.G. Hauck, W. Willing, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **534**, 77 (1986).
J.L. Hubbard and D.L. Lichtenberger, *Inorg. Chem.*, **19**, 1338 (1980).
K.K. Pandey, R.B. Sharma and P.K. Pandit, *Inorg. Chim. Acta*, **169**, 207 (1990).
K.K. Pandey, M. Massoudipour and V. Paleria, *Indian J. Chem.*, **29A**, 260 (1990).
M. Komorowska and R. Hoffman, *Inorg. Chem.*, **29**, 279 (1990).
A. Baba-Ahmed and I. Gayoso, *Theoret. Chim. Acta*, **62**, 507 (1983).
G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).
J. A. Pople and D. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, (1970).
R.S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
J.T. Veal and D.J. Hodgson, *Inorg. Chem.*, **11**, 1420 (1972).
T.S. Khodashova, M.A. Porai-Koshita, V.S. Sergienko, N.A. Parpiev and G.B. Bokii, *Zh. Struk. Khim.*, **13**, 1105 (1972).
A. Baba-Ahmed, J. Gayoso, B. Maouche and O. Ouamerali, *QCPE*, 474 (1985).
K.A. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
E. Mercer and A.B. Cox, *Inorg. Chim. Acta*, **6**, 577 (1972).
A.F. Leroy and J.C. Morris, *J. Inorg. Nucl. Chem.*, **33**, 473 (1971).
K.A. Bolshakav, N.M. Sinitsyn, V.V. Borisov and L.A. Zvorykina, *Russ. J. Inorg. Chem.*, **18**, 1435 (1973).
F. Bottomley and P.S. White, *Acta Cryst.*, **35B**, 2193 (1979).
J.T. Veal and D.J. Hodgson, *Acta Cryst.*, **28B**, 3525 (1972).
B.L. Haymore and J.A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).
A.J. Schultz, R.L. Henary, J. Reed and R. Eisenberg, *Inorg. Chem.*, **13**, 732 (1974).
F. Bottomley, *J. Chem. Soc., Dalton Trans.*, 1600 (1974).
S.H. Simonsen and M.H. Müller, *J. Inorg. Nucl. Chem.*, **27**, 309 (1965).
F. Bottomley, *J. Chem. Soc., Dalton Trans.*, 2538 (1975).
F. Bottomley, S.G. Clarkson and S.B. Tong, *J. Chem. Soc., Dalton Trans.*, 2344 (1974).
B. Czeska, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **498**, 121 (1983).