Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

	x	*y*	*z*	*U*[a]
I(1)	5987.5 (7)	2146.5 (8)	−355.0 (5)	59 (1)
I(2)	6454.9 (8)	4103.9 (8)	1569.5 (6)	70 (1)
Sm	4947.3 (4)	2575.7 (5)	1076.3 (3)	35 (1)
O(1)	4265 (6)	4143 (7)	538 (5)	61 (4)
O(2)	3611 (6)	2448 (8)	240 (5)	59 (4)
O(3)	3970 (7)	1038 (7)	1075 (6)	70 (4)
O(4)	5977 (7)	1158 (8)	1490 (6)	75 (5)
O(5)	5071 (7)	2114 (7)	2385 (5)	61 (4)
O(6)	3725 (7)	3142 (7)	1945 (5)	63 (4)
C(1)	4291 (11)	5047 (11)	832 (10)	96 (9)
C(2)	3580 (11)	4097 (11)	57 (8)	72 (7)
C(3)	3585 (11)	3161 (13)	−264 (8)	81 (8)
C(4)	3443 (11)	1512 (12)	10 (9)	83 (8)
C(5)	3260 (11)	928 (13)	602 (11)	99 (9)
C(6)	3858 (12)	420 (12)	1644 (10)	96 (9)
C(7)	6159 (14)	358 (14)	1099 (10)	111 (10)
C(8)	6187 (14)	1017 (15)	2160 (10)	112 (10)
C(9)	5892 (13)	1773 (13)	2571 (10)	101 (9)
C(10)	4656 (15)	2788 (15)	2823 (8)	98 (9)
C(11)	3805 (13)	2917 (15)	2626 (8)	93 (9)
C(12)	2854 (11)	3253 (18)	1754 (9)	119 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Distances and Angles for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

	(a) Bond Distances (Å)		
I(1)–Sm	3.322 (1)	I(2)–Sm	3.333 (1)
Sm–O(1)	2.692 (10)	Sm–O(2)	2.653 (9)
Sm–O(3)	2.660 (10)	Sm–O(4)	2.699 (11)
Sm–O(5)	2.689 (10)	Sm–O(6)	2.679 (10)
O(1)–C(1)	1.415 (19)	O(1)–C(2)	1.425 (19)
O(2)–C(3)	1.428 (20)	O(2)–C(4)	1.434 (20)
O(3)–C(5)	1.451 (22)	O(3)–C(6)	1.444 (21)
O(4)–C(7)	1.408 (23)	O(4)–C(8)	1.384 (22)
O(5)–C(9)	1.406 (22)	O(5)–C(10)	1.446 (22)
O(6)–C(11)	1.396 (20)	O(6)–C(12)	1.404 (20)
C(2)–C(3)	1.480 (24)	C(4)–C(5)	1.468 (26)
C(8)–C(9)	1.428 (28)	C(10)–C(11)	1.381 (29)
	(b) Bond Angles (deg)		
I(1)–Sm–I(2)	92.0 (1)	I(1)–Sm–O(1)	90.1 (2)
I(2)–Sm–O(1)	81.2 (2)	I(1)–Sm–O(2)	80.0 (2)
I(2)–Sm–O(2)	140.4 (2)	O(1)–Sm–O(2)	60.3 (3)
I(1)–Sm–O(3)	96.9 (2)	I(2)–Sm–O(3)	159.1 (2)
O(1)–Sm–O(3)	117.6 (3)	O(2)–Sm–O(3)	60.2 (3)
I(1)–Sm–O(4)	80.7 (2)	I(2)–Sm–O(4)	89.4 (2)
O(1)–Sm–O(4)	166.7 (3)	O(2)–Sm–O(4)	126.6 (3)
O(3)–Sm–O(4)	73.5 (3)	I(1)–Sm–O(5)	138.5 (2)
I(2)–Sm–O(5)	80.0 (2)	O(1)–Sm–O(5)	127.9 (3)
O(2)–Sm–O(5)	130.1 (3)	O(3)–Sm–O(5)	80.8 (3)
O(4)–Sm–O(5)	58.7 (3)	I(1)–Sm–O(6)	161.2 (2)
I(2)–Sm–O(6)	96.0 (2)	O(1)–Sm–O(6)	74.4 (3)
O(2)–Sm–O(6)	83.0 (3)	O(3)–Sm–O(6)	81.4 (3)
O(4)–Sm–O(6)	116.3 (3)	O(5)–Sm–O(6)	60.0 (3)
Sm–O(1)–C(1)	125.5 (10)	Sm–O(1)–O(2)	121.2 (8)
C(1)–O(1)–C(2)	109.9 (12)	Sm–O(2)–C(3)	114.4 (9)
Sm–O(2)–C(4)	113.8 (9)	C(3)–O(2)–C(4)	115.8 (12)
Sm–O(3)–C(5)	121.1 (9)	Sm–O(3)–C(6)	124.7 (9)
C(5)–O(3)–C(6)	110.6 (12)	Sm–O(4)–C(7)	123.8 (10)
Sm–O(4)–C(8)	122.6 (11)	C(7)–O(4)–C(8)	111.5 (14)
Sm–O(5)–C(9)	113.8 (9)	Sm–O(5)–C(10)	112.9 (9)
C(9)–O(5)–C(10)	118.0 (13)	Sm–O(6)–C(11)	119.5 (10)
Sm–O(6)–C(12)	122.1 (9)	C(11)–O(6)–C(12)	111.9 (13)
O(1)–C(2)–C(3)	109.1 (13)	O(2)–C(3)–C(2)	109.9 (13)
O(2)–C(4)–C(5)	108.0 (14)	O(3)–C(5)–C(4)	108.2 (14)
O(4)–C(8)–C(9)	111.5 (7)	O(5)–C(9)–C(8)	113.4 (16)
O(5)–C(10)–C(11)	109.7 (15)	O(6)–C(11)–C(10)	112.9 (15)

collected to the limit of availability. The intensity data were corrected for *Lp* effects and for absorption (empirical, ψ-scan, seven reflections, 252 data, six-parameter ellipsoid model).

The structure was solved by direct methods. All non-hydrogen atoms were refined with anistropic temperature factors. Hydrogen atom locations were idealized (d(C–H) = 0.96 Å) and updated as isotropic contributions. All computer programs were from the SHELXTL library (Version 5.1) distributed by the Nicolet Corp., Madison, WI.

Table II provides the atomic coordinates for **1**, and Table III the bond distances and angles. Additional data are available as supplementary material.

Acknowledgment. Support of this research through a grant from the National Science Foundation (No. CHE-8312380) to A.S. is gratefully acknowledged. The National Science Foundation also contributed funds for the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Stereoview of the unit cell packing for **1** (Figure S1) and tables of anisotropic thermal parameters (Table S1) and hydrogen atom coordinates (Table S2) for **1** (3 pages); a table of observed and calculated structure factors for **1** (Table S3) (11 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, Monash University, Clayton, Victoria 3168, Australia,
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, England,
Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia, and Institut für Anorganische und Analytische Chemie, Albert-Ludwigs Universität, 7800 Freiburg, Federal Republic of Germany

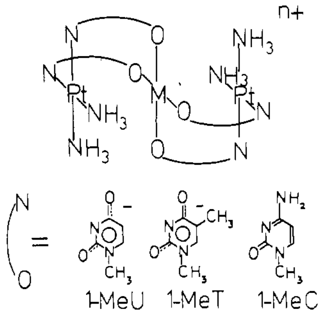
Magnetic Properties and Metal–Metal Interactions in Mixed-Metal (Pt_2M) Trimers (M = Ni, Co)

Darrell M. Duckworth,[†] David M. L. Goodgame,[‡] Michael A. Hitchman,[*§] Bernhard Lippert,[‖] and Keith S. Murray[*†]

Received November 7, 1986

Investigations of magnetic properties have often been used to provide information on the metal–metal interactions in polymeric transition-metal complexes.[1] This has almost always involved effects due to the coupling of the magnetic moments of paramagnetic metal ions, but the magnetic properties of some metal ions are quite sensitive to their ligand environment and this also has the potential to yield information on the effects that diamagnetic metal ions have on their paramagnetic neighbors in certain polymers. In particular, a recent study showed that the variation of the magnetic moments at low temperature caused by the zero-field splitting of the ground state can provide useful information about the nature of the ligand environment in low-symmetry Ni(II) complexes.[2]

As part of a general investigation of the ligating properties of pyrimidine nucleobases[3,4] we recently prepared a range of novel trimeric complexes of the form



where M = Cu(II), Ni(II), Co(II), Fe(II), and Mn(II). Here

---

[*] To whom correspondence should be addressed.
[†] Monash University.
[‡] Imperial College of Science and Technology.
[§] University of Tasmania.
[‖] Albert-Ludwigs Universität.

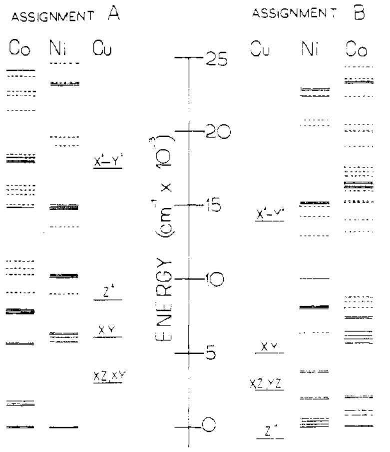


Figure 1. Two possible d-orbital energy sequences[5] A and B for the complex $Cu[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2 \cdot 6H_2O$, and the state energies of the analogous Co(II) and Ni(II) complexes (note that *orbital* energies are shown for the copper(II) compound and *state* energies for the cobalt(II) and nickel(II) complexes). High-spin levels are shown with full lines, and low-spin levels with dashed lines, where appropriate. The AOM metal–ligand bonding parameters of the Cu(II) complex are as follows: (A) $e_\sigma(xy) = 5850$ cm^{-1}, $e_\pi(xy) = 1530$ cm^{-1}, $e_\sigma(z) = 1386$ cm^{-1}; (B) $e_\sigma(xy) = 4643$ cm^{-1}, $e_\pi(xy) = 1250$ cm^{-1}, $e_\sigma(z) = -2602$ cm^{-1}. The values for the Co(II) and Ni(II) complexes are reduced by 10% and 20% in magnitude, respectively.

1-MeU = 1-methyluracil anion, 1-MeT = 1-methylthymine anion, and 1-MeC = 1-methylcytosine. The terminal Pt(II) ions complete a distorted octahedral arrangement of atoms about each central metal and may be considered to function as unusual, formally positively charged ligands. Analysis of the electronic spectra along these lines using the angular overlap model (AOM) suggested two possible scenarios for the bonding in the complexes.[5] The most probable interpretation implies that the Pt(II) ions act as weak σ-donors, while the second, less likely alternative would mean that they function as moderate σ-acceptors. In order to clarify the nature of the metal–metal interactions we have measured the temperature dependence of the magnetic susceptibilities of the 1-methyluracil Ni(II) and Co(II) trimers, and we report here the results of this study with an analysis that confirms the former interpretation of the electronic spectra.

Experimental Section

The preparation and characterization of the complexes $M[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2 \cdot 6H_2O$ (M = Ni and Co) has been given elsewhere.[6] The magnetic susceptibility of a powder of each complex was measured over the temperature range 295–4.25 K by using an Oxford Instruments Faraday balance operating with a field gradient of 1000 G/cm. Details of the calculations of magnetic moments have been given elsewhere.[7]

Results and Discussion

As reported previously,[5] the electronic spectrum of $Cu[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2 \cdot 6H_2O$ is consistent with two possible d-orbital energy sequences, as shown schematically in Figure 1. In one of these, A, the d_{z^2} orbital is raised slightly in energy by interaction with the filled $d_z{}^2$ orbital of each Pt(II) ion, while in the other, B, it is lowered by interacting with the empty p_z orbitals of the neighboring Pt(II) ions. Assuming identical metal–ligand bonding parameters to the Cu(II) compound, though reduced by 10% and 20%, respectively, implies the state energies indicated in Figure 1 for the corresponding Ni(II) and Co(II) complexes (*note that orbital energies are shown for the copper(II) compound and state energies for the cobalt(II) and nickel(II) complexes*). The *state energies* were calculated by using the computer program CAMMAG developed by Gerloch and co-workers.[8] These are very similar to those reported previously for the compounds,[5] except for the effects of spin–orbit coupling, which have been included in the present case. Condon–Shortley interelectron repulsion parameters $F_2 = 1360$ cm^{-1} and $F_4 = 102$ cm^{-1} were used in each case, as well as spin–orbit coupling constants of $\lambda = 400$ and 410 cm^{-1} for the Ni(II) and Co(II) complexes, respectively; the metal–ligand bonding parameters are given in the figure caption. As noted previously,[5] the reported band maxima in the range ~6000–24 000 cm^{-1} for the reflectance spectra of both the Ni(II) complex (6250, 10 100, 14 500, and 18 700 cm^{-1}) and the Co(II) complex (7750, 14 300, 17 400, and 23 500 cm^{-1}) agree well with the predictions of assignment A but are in poor agreement with those of assignment B (Figure 1).

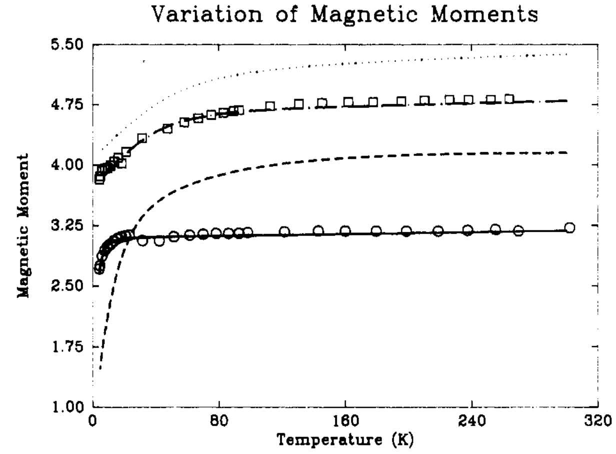


Figure 2. Experimental values of the magnetic moments of the nickel (circles) and cobalt (squares) ions in $M[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2 \cdot 6H_2O$, M = Ni and Co. The values calculated by the computer program CAMMAG are given by using the energy level assignments A (full line for Ni(II), dashed–dotted line for Co(II)), and B (dashed line for Ni(II), dotted line for Co(II)).

The variation of the magnetic moments of the Ni(II) and Co(II) ions in the two complexes over the temperature range 4.25 to 295K is shown in Figure 2. At room temperature the value of $\mu = 3.2$ μ_B observed for the nickel(II) compound is characteristic of a high-spin complex with an essentially octahedral ligand coordination geometry.[9] On cooling, the magnetic moment remains approximately constant until ~15 K, when it drops sharply (Figure 2). This behavior is just that expected for a ground state with a moderate zero-field splitting caused by a significant tetragonal component to the ligand field and is very similar to that reported recently for several complexes of the type $Ni(amine)_4X_2$, where X is a halide ligand[2]. Between 23 and 32K a slight discontinuity occurs in the variation of μ (Figure 2). This was found to be quite reproducible, and might be indicative of a phase change, though the electronic reflectance spectrum of the complex did not alter over this temperature range. The room-temperature value of the magnetic moment of the cobalt(II) compound, $\mu = 4.8$ μ_B, is characteristic of an octahedral complex with a ground state split by a highly distorted ligand field,[9] and this is confirmed by the temperature dependence of the moment, which shows that μ decreases progressively below ~120 K (Figure 2).

---

(1) See for example: Martin, R. L. *New Pathways in Inorganic Chemistry*, Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: Cambridge, England, 1968, ch. 9; Gleizes, A; Meyer, A.; Hitchman, M. A.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 2257 and references therein.

(2) Kennedy, B. J.; Murray, K. S.; Hitchman, M. A.; Rowbottom, G. L. *J. Chem. Soc. Dalton Trans.*, in press.

(3) Lippert, B.; Neugebauer, D.; Thewalt, U. *Inorg. Chem.* **1984**, *23*, 1713 and references therein.

(4) Schollhorn, H.; Thewalt, U.; Lippert, B. *J. Chem. Soc., Chem. Commun.* 1984, 769.

(5) Goodgame, D. M. L.; Hitchman, M. A.; Lippert, B. *Inorg. Chem.* **1986**, *25*, 2191.

(6) Goodgame, D. M. L.; Rollins, R. W.; Lippert, B. *Polyhedron* **1985**, *4*, 829.

(7) Mackey, D. J.; Evans, S. V.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1515.

(8) Cruse, D. A.; Davies, J. E.; Gerloch, M.; Harding, J. H.; Mackey, D. J.; McMeecking, R. F. *CAMMAG, a FORTRAN Computing Package*; University Chemical Laboratory: Cambridge, England, 1979.

(9) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966; ch. 10.

In order to see how the magnetic results conform to the two possible bonding schemes proposed for the complexes, the magnetic moments were calculated as a function of temperature by using the computer program CAMMAG. The only parameter required in this procedure in addition to the metal–ligand bonding parameters, interelectron repulsion parameters, and spin–orbit coupling constants used to estimate the energy levels in the complexes is an orbital reduction parameter k.[10] As may be seen from Figure 2, it was found that excellent agreement with the experimentally observed magnetic moments was obtained over the complete temperature range for both complexes using values of $k = 0.9$ and 0.95 for the Ni(II) and Co(II) complexes, respectively, with the metal–ligand bonding parameters appropriate to assignment A of the d-orbital energies (Figure 1). The relatively high values of k, which suggest that the bonding to the central metal ions is quite ionic, are consistent with the fact that the Co(II) and Ni(II) ions are surrounded by four oxygen ligand atoms and two distant Pt(II) ions.

The scheme A ascribes the steep decrease in μ at low temperature of the Ni(II) complex to a zero-field splitting of the ground state of 7 cm^{-1} caused by spin–orbit coupling to excited electronic states split by the substantial difference between the "ligand field" of the axial Pt(II) ions ($e_\sigma = 1247\ cm^{-1}$) and the in-plane oxygen ligands ($e_\sigma = 5265\ cm^{-1}$). In contrast, the gradual decrease in μ observed below ~120 K for the Co(II) complex is derived in this scheme from the splitting of the ground state by an amount comparable to normal thermal energies (Figure 1), this being caused by a combination of the tetragonal component of the ligand field and spin–orbit coupling.

For both complexes the magnetic moments calculated by using assignment B of the d-orbital energies are in very poor agreement with the observed values (Figure 2). In particular, for the nickel(II) complex, this scheme predicts a much larger value of the magnetic moment at room temperature than is observed experimentally, this being related to the very large tetragonal component of the ligand field implied by the bonding parameter of the axial Pt(II) "ligands" ($e_\sigma = -2342\ cm^{-1}$). This causes the E component of the ${}^3T_{2g}$ *state* of the parent octahedral complex to drop so substantially that it approaches the ground state in energy (Figure 1), producing a magnetic moment similar to that of a complex with an orbital triplet ground state.[9] Moreover, the very large zero-field splitting of the ground state predicted by scheme B (40 cm^{-1}) would suggest that on cooling the magnetic moment of the Ni(II) complex should start to decrease at a much higher temperature than is observed experimentally (Figure 2).

It is thus apparent that the magnetic measurements strongly support d-orbital energy sequences for the central metal ions in the trimers which imply that the terminal Pt(II) ions effectively function as normal ligands, producing weak antibonding interactions with the d orbitals that are consistent with the rather long metal–metal distances observed in the trimers (~270 pm).[3,11] The excellent agreement between the calculated magnetic moments and those observed experimentally, obtained without altering the bonding and interelectron repulsion parameters derived from the electronic spectra, illustrates both the value of carrying out magnetic measurements on compounds of this kind and the power of ligand field calculations performed with computer programs such as CAMMAG in interpreting the spectral and magnetic properties of transition-metal complexes.

Acknowledgment. The financial assistance of the Australian Research Grants Commission is gratefully acknowledged, and Dr. M. Gerloch, University Chemical Laboratory, Cambridge, England, is thanked for making available a copy of the computer program CAMMAG.

Registry No. $Ni[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2$, 97852-02-3; $Co[Pt(NH_3)_2(1\text{-}MeU)_2]_2(NO_3)_2$, 97851-99-5.

---

(10) Gerloch, M.; Miller, J. R. *Prog. Inorg. Chem.* **1968**, *10*, 1.
(11) Lippert, B; Schubert, U. *Inorg. Chim. Acta* **1981**, *56*, 15.

Contribution from the Pittsburgh Energy Technology Center,
Pittsburgh, Pennsylvania 15236

Metals for Which Crystalline Anhydrous Sulfates Are Not Known

Sidney S. Pollack

Received December 16, 1986

In the study of potential sorbents for the removal of SO_2 from flue gas, the question arose as to the formation of "molybdenum sulfate". After a short search, it became evident that no "molybdenum sulfate" had been reported in the literature. Further search identified other metals for which no data on simple anhydrous sulfates existed. All the alkali and alkaline earth metals, the first transition series, and metals from groups III–VI (groups 13–16)[13] except Ge form crystalline simple anhydrous sulfates. However, in the second and third transition series, all metals except Nb, Mo, Tc, Ru, Pd, W, Re, Os, Ir, Pt, and Au form simple sulfates. The positions of these elements in the periodic table relative to some of the metals in the first transition series are shown below to the left. On the right are shown the metals in the second and third transition series for which simple anhydrous phosphates are not known.

Sulfates									Phosphates					
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
	Nb	Mo	Tc	Ru		Pd				Tc	Ru	Rh	Pd	
	Ta	W	Re	Os	Ir	Pt	Au		W	Re	Os	Ir	Pt	Au

The statement that anhydrous sulfates are not known is based on the absence of simple anhydrous sulfates from the *Powder Diffraction File*[1] and from *Chemical Abstracts*. Molybdenum and niobium do not form simple anhydrous sulfates but do crystallize as the binary metal sulfate hydrates $K_3Mo_2(SO_4)_4\cdot3.5H_2O$,[2] $K_4Mo_2(SO_4)_4\cdot2H_2O$,[3] and $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot5H_2O$.[4] Size does not appear to be a critical factor, since there is an overlap in atomic radii between the elements that do and do not form anhydrous sulfates.[5]

Although $PdSO_4\cdot2H_2O$ and $Pt(SO_4)_2\cdot4H_2O$ are listed in the *Handbook of Chemistry and Physics*,[6] no structural information is available for these compounds. X-ray powder diffraction data have been reported for $Ta_2O_3(SO_4)_2\cdot0.5H_2O$,[7] but no structure has been described. The *Powder Diffraction File* lists even fewer simple anhydrous nitrates than sulfates and phosphates.[1] Addison and Logan summarized much information about anhydrous nitrates and showed a chart of the periodic table indicating the metals that form anhydrous metal nitrates.[8] They explained the absence of Ti, Nb, and Ta anhydrous nitrates on the basis that these metals would be expected to be present as covalent nitrates in their highest oxidation state. This would mean an unfavorable coordination number of five or a higher coordination number that would not be acceptable on steric grounds. They offered no explanation for the absence of the other simple anhydrous metal sulfates except osmium, which they indicated had not received a great deal of study. As of this work, no additional anhydrous nitrates have been reported.

Most of the metals that form anhydrous sulfates have an oxidation state of +2 or +3 except for the alkali metals, which have a +1 oxidation state. Titanium, which can have +1, +2, +3, and

---

(1) *Powder Diffraction File*; JCPDS International Center for Diffraction Data: Swarthmore, PA, 1985.
(2) Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Am. Chem. Soc.* **1973**, *95*, 4431.
(3) Angell, C. L.; Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Chem. Soc., Chem. Commun.* **1973**, 399.
(4) Bino, A. *Inorg. Chem.* **1982**, *21*, 1917.
(5) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.
(6) *Handbook of Chemistry and Physics*; CRC Press: Cleveland, OH, 1985.
(7) Maslennikova, R. D.; Chernyak, A. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1968**, *13*, 335.
(8) Addison, C. C.; Logan, N. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 71–142.