Main Group Metal Halide Complexes with Sterically Hindered Thioureas. IX.* New Complexes of Selected Post-transition Metals and 1,3-Dimethyl-2(3H)-imidazolethione and a Structural Investigation of Infrared Peak Shifts Associated with Coordination

DANIEL J. WILLIAMS**, PATRICIA H. POOR, GUILLERMO RAMIREZ and BARBARA L. HEYL

Department of Chemistry, Kennesaw College, Marietta, Ga. 30061, U.S.A.

(Received November 16, 1987)

Abstract

Five new complexes of sterically hindered 1,3-dimethyl-2(3H)-imidazolethione (dmit) with the chlorides of Cd(II), Hg(II), Te(II), Sn(IV) and Sb(V) have been synthesized and characterized. The previously reported Zn(II) adduct was also synthesized and further characterized. These complexes were of the general formula $MX_n(dmit)_m$ where $n = 2$ and $m = 2$ when M = Zn, Cd, Hg and Sn; and $n = 2$ and $m = 4$ for Te(II). The only 1:1 adduct observed was $SbCl_5dmit$, and its chemistry is more complex giving rise to unique redox products upon heating in solution. Solid state spectra of these complexes as well as for dmit complexes are reported and discussed with regard to the coordination sensitive N–C–N asymmetric stretch and the C=S stretch observed not only for dmit complexes but for tetramethylthiourea (tmtu) complexes reported in the literature as well. Greatest shifts on coordination are observed with the N–C–N asymmetric stretch for tmtu causing shifts to higher wave numbers ranging from 55 to 95 cm^{-1} relative to free tmtu. Shifts are explained on the basis of observed crystal structures of tmtu adducts showing a greater C–N double bond character. Dmit adducts show much smaller shifts both to higher and lower wave numbers for this mode relative to free ligand, and the C=S stretch shows little change also. Comparison to known crystal structures show little change in the bond distances of the dmit ligand upon coordination. Inductive effects based on correlations of shift magnitude to the Sanderson group electronegativity (SGEN) of the acceptor seem to be unrelated with the exception of a small positive correlation observed for the N–C–N asymmetric stretch of tmtu.

Introduction

There have been several infrared studies of thiourea-type complexes of main group metal halides

---

*Part VIII is ref. 1.

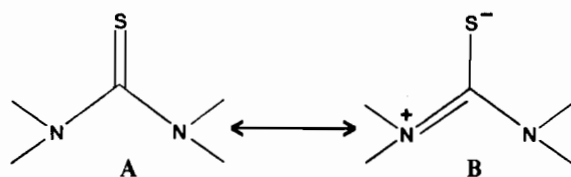**Author to whom correspondence should be addressed.

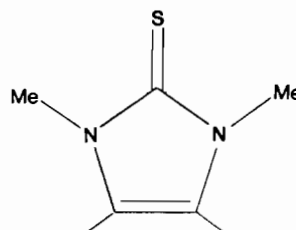Fig. 1. Characteristic resonance contributors for thioureas.

Fig. 2. Structure of 1,3-dimethyl-2(3H)-imidazolethione (dmit).

reported in the past [2–7]. Most studies dealing with both solid and solution state IR spectra in the 4000–400 cm^{-1} region have cited modes which were particularly sensitive to complexation and shifted in a predictable direction when going from the free state to the coordinated state. Two modes in particular have been used to demonstrate sulfur coordination — the C=S stretch and the N–C–N asymmetric stretch — the former usually decreasing in frequency, the latter usually increasing. Normally this behavior was rationalized on the structural basis as illustrated in Fig. 1 with the canonical form on the right (1B) being highly favored in sulfur coordination to a metal. Selvarajan [2] and Wharf et al. [3] noted this phenomenon in thiourea complexes of Zn(II), Cd(II) and Hg(II) while Gosavi and Rao [4] observed it for several metal complexes of a variety of alkylthioureas. Large shifts were noted particularly for the N–C–N asymmetric stretch in tetramethylthiourea (tmtu) complexes by Wynne et al. [5, 6], and Williams and Wynne [7] used this phenomenon to calculate solution state dissociation constants for $AsCl_3tmtu$ and $AsBr_3tmtu$ with quantitative IR by measuring concentrations of free coordinated tmtu

TABLE 1. Physical Properties and Analytical Data

	Melting point[a] (°C)	Appearance[b]	Λ[c]	C (%) Calc.	C (%) Obs.	H (%) Calc.	H (%) Obs.	N (%) Calc.	N (%) Obs.	Cl (%) Calc.	Cl (%) Obs.	MW in DMF Calc.	MW in DMF Obs.	λ_{max}[d]	^{1}H NMR[e] δ (CH$_3$)	δ (ethyl)
SbCl$_5$dmit[f]	153–155	ye cr	253	16.09	16.31	2.47	2.20	7.82	7.59	39.59	38.49	427	g	206	3.75	7.65
ZnCl$_2$(dmit)$_2$	197–200	wh cr	11.0	30.59	30.65	4.11	4.13	14.27	14.27	18.06	18.13	393	126	262	3.62	6.96
CdCl$_2$(dmit)$_2$	>300	wh cr	19.7	27.32	27.37	3.67	3.73	12.74	12.71	16.13	16.05	440	g	262	3.51	6.80
HgCl$_2$(dmit)$_2$	225d	ye wh cr	18.3	22.75	22.81	3.06	3.03	10.61	10.59	13.43	13.35	528	g	263	3.64	6.99
SnCl$_4$(dmit)$_2$	285d	ye cr	19.0	23.24	23.36	3.12	3.17	10.84	11.04	27.43	27.25	517	182	261	3.81	7.13
TeCl$_2$(dmit)$_4$[h]	150d	vt cr	12.0	29.98	29.79	5.29	5.28	13.98	13.86	8.85	8.81	711	g	277 {358}	3.51	6.80

[a]Uncorrected. [b]Key: wh, white; ye, yellow; vt, violet; cr, crystals. [c]Acetontrile. Units: cm^2 eq^{-1} ohm^{-1}; ca. 10^{-3} M. [d]Reported in nm for saturated CH$_3$CN solutions; ϵ_{max} not computed. [e]In CD$_3$CN. Shifts reported in ppm (δ) relative to internal TMS. [f]Isolated as SbCl$_5$dmit. [g]Too insoluble for study. [h]Isolated as TeCl$_2$-(dmit)$_4$·5H$_2$O; %H$_2$O lost after 2 h heating at 140°C = 11.61%, calc. 11.24%.

at 1505 and 1959 cm^{-1}, respectively. Only one thiourea studied — 1,3-dimethyl-2(3H)-imidazolethione (dmit, Fig. 2) — gave shifts for these modes which were relatively small (0–25 cm^{-1}) [7, 8].

The purpose of this paper is to report the synthesis and characterization of five new dmit complexes of selected post-transition metals and to further investigate changes in IR frequencies for complexes containing sterically hindered thioureas — specifically tmtu and dmit — relating these changes to actual solid state crystallographic data already reported in the literature. In addition, this paper reports a more detailed characterization of ZnCl$_2$-(dmit)$_2$ [8]. We also report observed trends in shift magnitude relative to Sanderson group electronegativity (SGEN) of the acceptor molecule.

Experimental

General

Specific conductivity, solid state infrared data, and other physical characterizations were all obtained as previously reported [1, 9]. Ultraviolet spectra were recorded on a Varian DMS-90 UV—Vis spectrophotometer in CH$_3$CN in 1 cm quartz cells. Only λ_{max} values were recorded. Proton NMR data were obtained in CD$_3$CN on a Perkin-Elmer Model R-20 60 MHz spectrometer. Shifts are reported in ppm (δ) relative to internal Me$_4$Si.

Chemicals

All chemicals were used as commercially obtained without further purification. Spectral grade solvents (Fisher) were used after storage over Linde 4 Å molecular sieves. dmit was synthesized according to previously reported literature methods [10].

Synthesis

The dmit complexes of Zn(II), Cd(II) and Hg(II) chlorides were obtained by mixing stoichiometric quantities of the appropriate halide and dmit in boiling methanol. Recrystallization was accomplished in hot CH$_3$CN. The Te(II) complex was synthesized according to the method reported by Foss and Fossen [11], and the complexes of Sb(V) and Sn(IV) chlorides were synthesized in a glovebag under a dry nitrogen atmosphere after a manner previously reported by Williams and Wynne [7]. Hot CH$_3$CN was the recrystallizing solvent although prolonged exposure of SbCl$_5$dmit to the hot solvent resulted in the generation of [dmit$_2$][SbCl$_4$]$_2$ as verified via chemical composition and X-ray crystallographic data [12].

Analytical

Elemental analysis was done by Atlantic Microlabs, and molecular weights in DMF were determined by Galbraith Laboratories, Inc.

Results and Discussion

Table I lists physical and chemical parameters measured for the new complexes. The new complexes generated were all air-stable solids which all displayed relatively low solubility in various solvents both polar and non-polar. Acetonitrile and *N,N*-dimethylformamide appeared to be the best solvents for solution characterization purposes. The Te(II) salt decomposed in aqueous solutions yielding elemental Te similar to other thiourea derivatives of this particular type [11]. The extremely high melting point of the Cd(II) complex implies either an ionic or polymeric structure in the solid state, and based on solution state conductivity studies, it's more than likely polymeric perhaps similar in structure to $Cd(SCN)_2(etu)_2$ (etu = ethylene thiourea) [13].

Solution state studies reveal all but the Sb(V) complex to be non-electrolytes, and it is more than likely that the observed value for the Sb(V) complex is actually that of the dithiouronium salt since it falls into the range of a 2:1 electrolyte [14]. Prolonged heating was required to dissolve the complex in order to obtain the 10^{-3} M solution, and as explained above this results in the formation of the disulfide salt. Interestingly, the Te(II) complex should be an electrolyte based on known solid state structures reported for several thiourea analogs. The ethylene thiourea (etu) complex, for example, contains the square-planar $[Te(etu)_4]^{2+}$ cation in the solid state [15], and several other crystallographic structures of other thiourea analogs have shown similar results [11, 15]. It is possible that tight-ion pair formation or some type of radical structural change in solution is responsible for the non-electrolyte behavior in solution.

The observed UV absorptions of the complexes for Zn(II), Cd(II), Hg(II) and Sn(IV) show a slight hypsochromic shift relative to the free ligand which gave an observed maximum wavelength at 272 nm in acetonitrile (*cf.* 260 nm in EtOH [8]. This is characteristic of an $n \rightarrow \pi^*$ transition in regard to shift direction with change in solvent polarity or coordination to a metal [16]. The UV data taken together with the proton NMR data and the limited molecular weight data seem to indicate a high degree of dissociation at least for the Zn(II), Cd(II) and Hg(II) complexes. Small differences in the chemical shifts for the methyl protons relative to uncoordinated dmit are observed for these three metal complexes whereas the Sn(IV) complex shows a larger shift implying at least a larger degree of association along with the increased inductive effect due to the higher oxidation state (*cf.* CH_3 shift for uncomplexed dmit in acetonitrile is 3.51 [7].

The observed NMR shift and λ_{max} for $SbCl_5$dmit support the fact that the compound has been altered upon prolonged heating to obtain sufficiently concentrated solutions for study, and the Te(II) complex appears to be completely dissociated based on the NMR data, thus indicating perhaps some type of structural change if indeed the solid state structure is ionic as presumed based on literature precedence. The UV maximum is also nearest to the uncomplexed value for dmit supporting a molecular dissociative process as opposed to ionic.

With regard to the solid state vibrational data and the question of coordination sensitive modes related to structure, Table II lists frequency shifts of $\nu(N-C-N)_{asym}$ and $\nu(C=S)$ as well as the direction of frequency shift relative to the uncomplexed ligand for several tmtu and dmit complexes. Sanderson group electronegativities (SGEN) for the acceptors are also listed [17]. Table III lists average bond distances as calculated from several reported X-ray crystallographic studies containing dmit and tmtu ligands [8, 19–27], and structural information for the free ligands is also included [10, 24]. Changes in angles are not included in this table since they have already been discussed in an earlier work [7] for dmit.

The largest changes are noted for the N–C–N asymmetric stretch of tmtu, and can be rationalized based on the overall shortening of the C–N bond upon complexation (1.39 Å for free tmtu *versus* 1.34 Å for the complexed ligand). Unfortunately not many reports for the C=S stretch for tmtu adducts are found in the literature. As we can see, however, from the few values in Table II, the shift is not as great as one would expect based on the relatively large elongation of 0.07 Å in the C=S bond in the complexed state. Gosavi and Rao [4] noted the small change in C=S stretching frequency upon complexation and explained that the change in C=S bond order is compensated through coupling with other vibrations such that the stretching frequency remains relatively unaltered. Nevertheless, these changes substantiate the assertion that complexation favors the increase in bond order of the C–N bond and decreases that of the C=S bond as seen in Fig. 1B.

Very small shifts are observed in both modes for the dmit ligand, and inspection of Table III will reveal very little significant change in the ring structure and the C=S bond length between the free and complexed states. The already-favored 'aromatic' structure of the ring alters very little upon complexation, thus changes in frequencies are small.

To investigate inductive effects on magnitude of shift, we plotted SGEN values *versus* changes in shifts relative to the uncoordinated ligand for the N–C–N asymmetric stretches of tmtu and dmit, and also for the C=S stretch of dmit. No clear-cut trend could be observed although as seen in Fig. 3 for tmtu, there is a slight trend toward higher SGEN

TABLE II. Stretching Frequency Shifts for Coordination Sensitive Modes in dmit and tmtu Complexes (cm^{-1})[a]

Compound	$\Delta\nu$(N–C–N)asym	$\Delta\nu$(C=S)	SGEN	Reference
AsCl$_3$dmit	−15	+10	4.65	7, 18
AsBr$_3$dmit	−20	+10	4.37	7, 18
PhAsBr$_2$(dmit)$_2$	−5	−5	4.32	7
AsI$_3$dmit	−10	−5	3.86	18
BiCl$_3$(dmit)$_2$	−5	−5	4.41	18
BiBr$_3$dmit	−20	−10	4.13	18
BiI$_3$(dmit)$_3$	−10	−15	3.66	18
CdCl$_2$(dmit)$_2$	0	−5	3.98	b
CoCl$_2$(dmit)$_2$	c	−7	3.72	8
CoBr$_2$(dmit)$_2$	c	−10	3.60	8
CoI$_2$(dmit)$_2$	c	−10	3.28	8
HBr(dmit)	+10	c	4.01	8
HgCl$_2$(dmit)$_2$	−5	−5	4.14	b
NiCl$_2$(dmit)$_2$	c	−5	3.72	8
NiBr$_2$(dmit)$_2$	c	−5	3.57	8
NiI$_2$(dmit)$_2$	c	−5	3.28	8
PbCl$_2$(dmit)$_2$	0	+10	4.21	1
Pb(NCS)$_2$(dmit)$_2$	−5	0	2.84	1
TeCl$_2$(dmit)$_4$	−10	−15	4.45	b
SbCl$_3$dmit	−15	+5	4.48	18
SbBr$_3$dmit	−10	+5	4.20	18
SbI$_3$dmit	−10	+5	3.72	18
SbCl$_5$dmit	−20	0	4.62	b
SnCl$_4$(dmit)$_2$	−5	−5	4.49	b
ZnCl$_2$(dmit)$_2$	0(c)	0(−8)	4.10	b (8)
ZnBr$_2$(dmit)$_2$	c	−9	3.81	8
ZnI$_2$(dmit)$_2$	c	−9	3.54	8
AsCl$_3$tmtu	−10	+90	4.65	7
AsBr$_3$tmtu	−5	+93	4.37	7
PhAsCl$_2$tmtu	d	+86	4.32	7
PhAsBr$_2$tmtu	d	+85	4.14	7
PhAsI$_2$tmtu	d	+61	3.81	7
p-CH$_3$PhAsCl$_2$tmtu	d	+84	4.32	7
p-CH$_3$PhAsBr$_2$tmtu	d	+95	4.14	7
p-CH$_3$PhAsI$_2$tmtu	d	+78	3.81	7
p-CH$_3$OPHAsCl$_2$tmtu	d	+68	4.35	7
p-ClPhAsCl$_2$tmtu	d	+86	4.32	7
p-NO$_2$PhAsCl$_2$tmtu	d	+85	4.40	7
CdeCl$_2$tmtu	−1	+62	3.98	4
HgCl$_2$tmtu	−3	+84	4.14	4
PdCl$_2$tmtu	−2	+85	3.82	4
SeCl$_2$tmtu	c	+90	4.69	6
SeBr$_2$tmtu	c	+85	4.43	6
MeTeCl$_3$tmtu	c	+70	4.35	5
MeTeBr$_3$tmtu	c	+70	4.14	5
MeTeI$_2$tmtu	c	+55	3.74	5
EtTeCl$_2$tmtu	c	+95	4.36	5
EtTeBr$_3$tmtu	c	+65	4.14	5
EtTeI$_3$tmtu	c	+67	3.75	5
p-CH$_3$OPhTeCl$_3$tmtu	c	+55	4.39	5

[a]Observed ν(N–C–N)$_{asym}$ and ν(C=S) frequencies for uncoordinated ligands (cm^{-1}) respectively: dmit = 1570, 1170–1180 [7, 8]; tmtu = 1495–1505, 1060 [4, 7]. [b]This study. [c]Not reported. [d]Obscured by phenyl modes.

values being related to greater shifts to higher wave-numbers for the N–C–N asymmetric stretch, but just the reverse trend is noted for the same mode in dmit (Fig. 4). Based on the structural data already presented, this can be rationalized on the basis of more intensified charge separation due to stronger electron-withdrawing acceptors in tmtu as illustrated by Fig. 1B. The relationship for dmit, however, is

TABLE III. Comparison of Bond Distances in Uncoordinated (U) and Coordinated (C) dmit [8, 19–23] and in Uncoordinated (U) and Coordinated (C) tmtu [24, 27][a]

	C=S	C–N	N–Me	Other
dmit$_U$	1.79(1)	1.35(1)	1.45(1)	1.39(1) N–C(ring)
dmit$_C$	1.72(1)	1.36(2)	1.48(7)	1.38(2) N–C(ring)
tmtu$_U$	1.67(1)	1.39(1)	1.46(1)	
tmtu$_C$	1.74(3)	1.34(4)	1.47(6)	

[a]All values are in Å with e.s.d.s in parentheses.
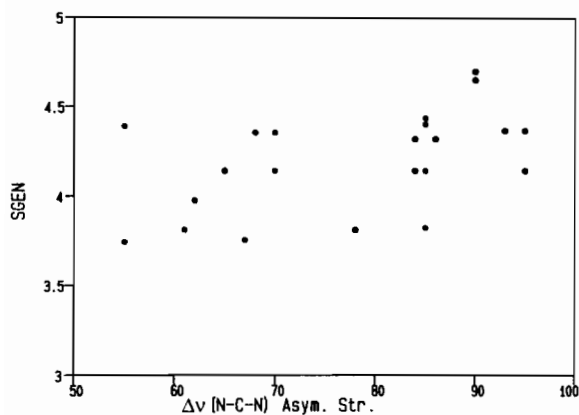
Fig. 3. Sanderson group electronegativity (SGEN) vs. frequency shifts ($\Delta\nu$) in cm^{-1} relative to uncoordinated ligand for the N–C–N asymmetric stretch of tmtu. Data given in Table II.
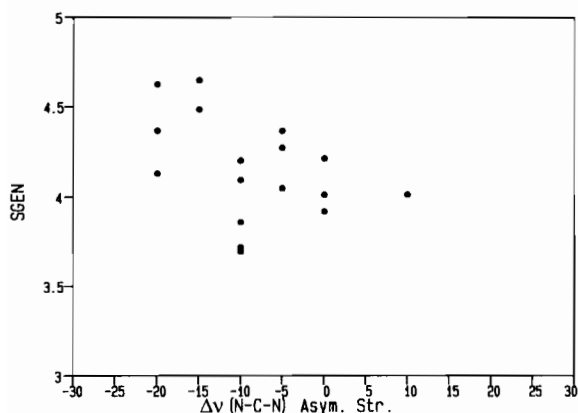

Fig. 4. Sanderson group electronegativity (SGEN) vs. frequency shifts ($\Delta\nu$) in cm^{-1} relative to uncoordinated ligand for the N–C–N asymmetric stretch of dmit. Data given in Table II.

not as easily rationalized, but electron-withdrawing acceptors apparently tend to slightly reduce the bond order in the dmit ring thus suggesting some minor perturbation to its aromatic character albeit not evident through comparison of bond distances in Table III. The relationship between SGEN and C=S stretch also suggests a reverse trend over what would
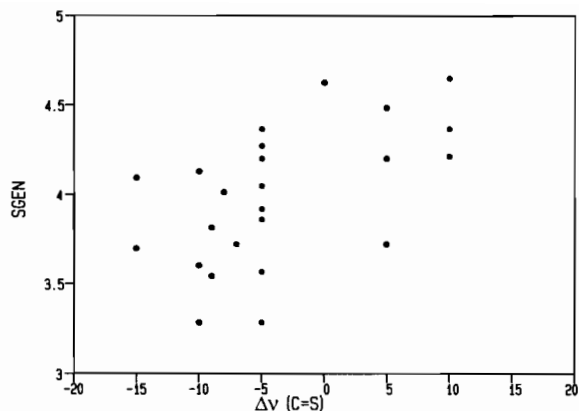

Fig. 5. Sanderson group electronegativity (SGEN) vs. frequency shifts ($\Delta\nu$) in cm^{-1} relative to uncoordinated ligand for the C–S stretch of dmit. Data given in Table II.

be expected where stronger electron-withdrawing groups tend to increase the bond order (Fig. 5). The majority of shifts are relatively small for dmit, and bordering of the edge of experimental error. Given the small shifts and the virtually unchanged structure of the ligand on complexation, the inductive effect of the acceptors coordinated to dmit seems to have little or no relationship to the magnitude of shift.

In conclusion, typical indicators for complexation in thioureas such as the C=S stretch or the N–C–N asymmetric stretch tend not to be reliable with dmit since the magnitude and direction of shift relative to the uncomplexed ligand tend to be relatively small and unrelated to the nature of the acceptor. This is in contrast to the acyclic, non-aromatic alkyl thioureas such as tmtu, in which at least the N–C–N asymmetric stretch tends to be a good indicator, and tends to fit a pattern of greater shift to higher wavenumbers with increased electronegativity of the acceptor. Structural comparisons between complexed and uncomplexed ligands give evidence for the reason for such observations with significant structural difference noted for tmtu while dmit remains virtually unchanged.

Acknowledgements

References

1 D. J. Williams, P. H. Poore and R. L. Jones, *Inorg. Chim. Acta, 144*, 237 (1988).

2 A. Selvarajan, *Ind. J. Pure Appl. Phys.*, *8*, 338 (1970).

3 I. Wharf, T. Gramstad, R. Makhija and M. Onyszchuk, *Can. J. Chem.*, *54*, 3430 (1976).

4 R. K. Gosavi and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, *29*, 1937 (1967).

5 K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, *10*, 2735 (1971).

6 K. J. Wynne, P. S. Pearson, M. G. Newton and J. Golen, *Inorg. Chem.*, *11*, 1192 (1972).

7 D. J. Williams and K. J. Wynne, *Inorg. Chem.*, *17*, 1108 (1978).

8 N. Kheddar, J. Protas, M. LeBaccon, R. Guglielmetti and J. Guerchais, *Bull. Chim. Soc. Fr.*, 803 (1976).

9 D. J. Williams and A. Viehbeck, *Inorg. Chem.*, *18*, 1823 (1979).

10 G. B. Ansell, D. M. Forkey and D. W. Moore, *Chem. Commun.*, 56 (1970).

11 O. Foss and S. Fossen, *Acta Chem. Scand.*, *15*, 1620 (1961).

12 D. J. Williams, P. H. Poor, G. Ramirez, B. L. Heyl and D. VanDerveer, unpublished results.

13 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon Press, Oxford, 1984, p. 1412.

14 W. J. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).

15 R. C. Elder, T. Marcuso and P. Boolchand, *Inorg. Chem.*, *16*, 2700 (1977).

16 D. A. Skoog, 'Principles of Instumental Analysis', 3rd edn., Saunders, New York, 1985, p. 186.

17 R. T. Sanderson, 'Inorganic Chemistry', Reinhold, New York, 1967, p. 81.

18 D. J. Williams, unpublished results.

19 D. J. Williams, M. G. Newton and K. J. Wynne, *Cryst. Struct. Commun.*, *6*, 167 (1977).

20 D. J. Williams, C. O. Quicksall and K. J. Wynne, *Inorg. Chem.*, *17*, 2071 (1978).

21 D. J. Williams, B. Rubin, J. Epstein, W. K. Dean and A. Viehbeck, *Cryst. Struct. Commun.*, *11*, 1 (1982).

22 B. Rubin, F. J. Heldrich, W. K. Dean, D. J. Williams and A. Viehbeck, *Inorg. Chem.*, *20*, 4434 (1981).

23 D. J. Williams, G. Ramirez and D. VanDerveer, *J. Crystallogr. Spectrosc. Res.*, *16*, 309 (1986).

24 E. Hough and D. G. Nicholson, *J. Chem. Soc., Dalton Trans.*, 2083 (1981).

25 S. Esperas, J. W. George, S. Husebye and O. Mikalsen, *Acta Chem. Scand., Ser. A*, *29*, 141 (1975).

26 K. Ase and I. Roti, *Acta Chem. Scand., Ser. A*, *28*, 104 (1974).

27 K. J. Wynne, P. S. Pearson, M. G. Newton and J. Golen, *Inorg. Chem.*, *11*, 1192 (1972).