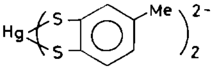
The Metal NMR Spectra of Thiolate and Phenylselenolate Complexes of Zinc(II) and Mercury(II)

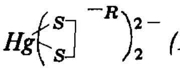
GEETHA K. CARSON and PHILIP A. W. DEAN*

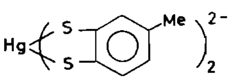
Department of Chemistry, University of Western Ontario, London, Ont., N6A 5B7, Canada

Received November 11, 1981

Soluble thiolato–zincates and –mercurates(II) of the general type $M(SR)_4^{2-}$ *and the phenylselenolato complexes* $M(SePh)_4^{2-}$ *(M = Zn or Hg) have been prepared* in situ *from the appropriate metal nitrate and excess thiolate or selenolate. The high field metal NMR spectra of these complexes have been measured, at 25.0 and 71.5 MHz for* ^{67}Zn *and* ^{199}Hg *respectively, with isotopic enrichment to 89.7 atom% for* ^{67}Zn*, but at natural abundance for* ^{199}Hg*. The zinc complexes studied in* D_2O *solution, were* $Zn(SR)_4^{2-}$ *(R = Me,* Pr^i*, or Ph),* $Zn(\overset{S}{\underset{S}{\langle}}])_2^{2}$ *and* $Zn(SePh)_4^{2-}$*. The variation of* δ_{Zn} *with ligand was found to be* $^-SePh < {}^-SPh < {}^-Spr^i < {}^-SMe < {}^-S(CH_2)_2S^-$*, as has been found earlier for* ^{113}Cd *also; the shifts for solutions in which* $[Zn]_{total} = 0.15$ M*, to higher frequency than the resonance of 2m* $Zn(ClO_4)_2$ *at 297 K range from 224 to 418 ppm, and the approximate linewidths from* ca. *55 Hz for* $Zn(SMe)_4^{2-}$ *at 368 K to* ca. *1200 Hz for* $Zn(SPr^i)_4^{2-}$ *at 297 K or* $Zn(\overset{S}{\underset{S}{\langle}}])_2^{2-}$ *at 363 K. The line widths appear to be the major factor limiting the application of* ^{67}Zn *NMR towards complexes of less symmetrical thiolates; rapid chemical exchange is not a problem, as* ^1H *and* ^{13}C *NMR studies of the zinc complexes show them to be less labile than their cadmium analogs. Conversely the mercury complexes studied here*



 *(R = H, Me, Et, or* CH_2OH*),* $Hg(SR)_4$ *(R = M=, Et,* Pr^i*, or Ph) and* $Hg(SePh)_4^{2-}$*) are more labile than their cadmium counterparts, and this lability reduces the utility of* ^{199}Hg *NMR in cases where multiple mercury-binding sites are available. The overall variation of* δ_{Hg} *with ligand,* $^-SePh < {}^-SPh < {}^-SR$ *(R = alkayl) < chelating vicinal dithiolates, is the same as found in the metal NMR of the corresponding zinc and cadmium complexes, but the (relatively small) effects of alkyl substitution are dissimilar. For* ca. *0.1* M *solutions in 1:1 (v:v)* H_2O*:* D_2O *at 297 K, the* ^{199}Hg *chemical shifts to higher frequency than the signal of 0.1* M $Hg(ClO_4)_2$ *in 5% (v:v)* $HClO_4$ *range from 1275 ppm in* $Hg(SePh)_4^{2-}$ *to 2234 ppm for*



the linewidths are relatively sharp (e.g. *≲4 Hz for* $Hg(SMe)_4^{2-}$*, ≲75 Hz for* $Hg(SPh)_4^{2-}$*).*

Introduction

Recently, we have reported the ^{113}Cd NMR spectra of a wide range of simple thiolatocadmates [1], as well as the ^{113}Cd and ^{77}Se NMR spectra of all five complexes in the series $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ [2]. These studies of model complexes were intended to provide background data for the interpretation of the ^{113}Cd NMR spectra of more complicated biologically important cadmium complexes, especially cadmium metallothionein [3–6], and in the assessment of the NMR spectral changes which might be expected if selenolates are formed and bind to cadmium following antidotal selenite treatment of cadmium intoxicated rats [7–9, 10a].

Native cadmium metallothionein always contains appreciable amounts of zinc (*e.g.* Refs. 11–13) and is thus the mixed metal thionein cadmium, zinc metallothionein (Zn, Cd–MT). Similarly native mercury metallothionein contains zinc and is at least Zn, Hg–MT (*e.g.* Ref. 12). As each of the Group IIB elements has at least one magnetically active isotope (^{67}Zn, 4.11% natural abundance, spin I = ½; ^{111}Cd, 12.75% natural abundance, spin I = ½; ^{113}Cd, 12.26% natural abundance, spin I = ½; ^{199}Hg, 16.84% natural abundance, spin I = ½) for which NMR has been observed, these and other, synthetic (*e.g.* Cd, Hg–MT) mixed metal metallothioneins might eventually prove suitable candidates for scrutiny by multimetal NMR. As a prelude to such studies we have extended our earlier work on thiolatocadmates [1] to the metal NMR of a range of

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$0.275

model thiolatocomplexes of zinc and mercury. In addition, for comparison with the ^{113}Cd NMR spectrum of $Cd(SePh)_4^{2-}$ [2], we have measured the metal NMR spectra of soluble complexes of zinc and mercury with $PhSe^-$ as a ligand. The ^{199}Hg chemical shift in the mercuric–selenolate complex is of interest as a possible indicator of the shift to be expected if mercury becomes directly bound to selenium when selenite is administered to diminish the effects of acute and chronic inorganic mercury poisoning of rats [9, 10b, 14].

Experimental

Materials

Zinc and mercury(II) perchlorates, from Alfa Products, cadmium nitrate (certified grade) from Fisher Scientific Co., and mercury(II) nitrate (Analar grade) from BDH Chemicals Ltd., were used as received. Zinc-67 enriched ZnO (89.7 atom% ^{67}Zn), from Oak Ridge National Laboratory, was converted to $Zn(NO_3)_2 \cdot 6H_2O$ for use in the NMR study. Phenylselenol and the various thiols were those used in our previous work [1, 2]. D_2O (≥99.7 atom% D) was obtained from Merck Sharpe and Dohme Canada.

Preparation of $(Me_4N)_2[M(SPh)_4]$ (M = Cd or Hg) and $(Me_4N)_2[Hg(tdt)_2]$ *

These thiolato complexes were synthesized in a manner analogous to that used by Dance [15] to prepare $(Me_4N)_2[Co(SPh)_4]$. Under N_2, phenylthiol (32 mmol) or, for the tdt^{2-} complex, 3,4-toluenedithiol (16 mmol), tri-*n*-butylamine (24 mmol), Me_4NCl (20 mmol) and the appropriate metal nitrate (3.4 mmol) were mixed in deaerated MeOH. Deaerated Bu^nOH was added to lower the solubility of the desired complexes which crystallized on cooling. All were colourless. *Anal.* Calcd. for $(Me_4N)_2[Cd(SPh)_4]$, $C_{32}H_{44}CdN_2S_4$: C, 55.11; H, 6.36; N, 4.02. Found: C, 55.30, 55.19, H, 6.37, 6.14; N, 3.91, 3.91%. Calcd. for $(Me_4N)_2[Hg(SPh)_4]$, $C_{32}H_{44}HgN_2S_4$; C, 48.93; H, 5.65; N, 3.57. Found· C, 49.60; H, 5.87; N, 3.71%. Calcd. for $(Me_4N)_2[Hg(tdt)_2]$· C, 40.20; H, 5.52; N, 4.26. Found. C, 39.88, 39.85; H, 5.25, 5.76; N, 4.96, 5.03%.

NMR Sample Preparation

Samples were prepared in capped or (for the $PhSe^-$ complexes) flame-sealed standard 10 mm od NMR tubes using the inert atmosphere procedures detailed previously [1, 2].

NMR Spectra

Proton and proton-decoupled carbon-13 NMR spectra were obtained in the manner described earlier [1] using a Varian XL-100-12 Spectrometer System operating at 100.10 and 25.20 MHz (at the TMS resonance) for ^{1}H and ^{13}C, respectively.

Zinc-67 and ^{199}Hg NMR spectra were obtained using a Bruker WH-400 Spectrometer operating at 25.04 and 71.51 MHz (at the reference signal), respectively. With $[^{67}Zn]_{total} \approx 0.15$ *M* the ^{67}Zn NMR spectra of the tetrakis(methanethiolato)–zincate, which gave a comparatively sharp line, were obtained using 250 to 750 90° (100 μs) pulses at 73 min^{-1} with an acquisition time of 0.819s and a spectral window of 5 kHz. The broader ^{67}Zn resonances of the other thiolato–zincates were evident after acquisition of 1000–2000 transients using 90° pulses at 293 min^{-1} with an acquisition time of 0.205s and a spectral window of 10 kHz, provided several (usually 6) points of the accumulated FID were discarded to alleviate baseline distortion which was particularly troublesome in these cases. With [Hg] ≈ 0.10 *M*, satisfactory ^{199}Hg NMR spectra could be obtained with about 100 90° (55 μs) pulses applied at 73 min^{-1} with an acquisition time of 0.819 s and a 10 kHz spectral window.

The ^{67}Zn NMR spectra were referenced to 2m $Zn(ClO_4)_2$ in D_2O, and the ^{199}Hg NMR spectra to 0.1 *M* $Hg(ClO_4)_2$ in 5% (v/v) $HClO_4$ solution, by sample interchange. No corrections for susceptibility differences were applied. Shifts to higher frequency than the reference are taken as positive.

Elemental Microanalysis

These were performed by Guelph Chemical Laboratories Ltd.

Results and Discussion

Preparation of the Thiolato–Zincates and –Mercurates in Solution

Addition of RE^- (E = S, various R: E = Se, R = Ph) to zinc or mercuric nitrate in methanol or water results in precipitate formation up to $RE^-/M \approx 2$ Compounds of the general type $(RS)_2M$ are well established for both zinc (*e.g.* Refs. 16–18) and mercury (*e.g.* Refs. 17–19), and $(PhSe)_2Hg$ is known also [20, 21]; apparently the analogous $(PhSe)_2Zn$ can be formed under the present conditions. Addition of excess RE^- results in dissolution of the precipitate for all the cases studied here. These solutions, normally containing (total RE^-)/$M^{2+} \approx 12$ (to prevent formation of polynuclear thiolate-bridged species [22]), were scrutinized by NMR. We were able to confirm that the ZnS_4 kernel, which is present in $(Ph_4P)_2[Zn(SPh_4]$ in the solid state [23, 24], persists in solution under our conditions (see below). Although it was not possible to confirm directly the occurrence of the HgS_4 kernel in solution (see below), we have assumed its presence because we (see Experimental Section) and others [25] have

---

*tdt^{2-} = toluene-3,4-dithiolate.

TABLE I. Zinc-67 NMR Spectral Parameters of Some Thiolatozincates and $Zn(SePh)_4^{2-}$ [a].

Complex	T (K)	δ_{Zn} (ppm)[b]	Approximate $\nu_{1/2}$ (Hz)
$Zn(SMe)_4^{2-}$ [c]	297	362	110
$Zn(SMe)_4^{2-}$ [c]	368	354	55
$Zn(SMe)_4^{2-}$	297	359	180
$Zn(SMe)_4^{2-}$ [d]	297	357	260
$Zn(SPr^i)_4^{2-}$	297	352	1200
$Zn(SPr^i)_4^{2-}$	368	303	420
$Zn(SPh)_4^{2-}$	303	267	1050
$Zn(SPh)_4^{2-}$	363	261	450
$Zn(^{S}_{S}])_2^{2-}$ [e]	363	418	1200
$Zn(SePh)_4^{2-}$	363	224	830

[a] Measured at 25.04 MHz using D_2O solutions where (total thiol or selenol) $Zn(NO_3)_2$: NaOH = 12·1:18 and $[Zn]_{total}$ = 0.15 *M* with 89.7 atom ^{67}Zn, except where noted. [b] Relative to 2m $Zn(ClO_4)_2$ at 297 K; shifts to higher frequency than the reference are taken as positive. [c] MeSH $Zn(NO_3)_2$:NaOH = 12·1 12. [d] MeSH:$Zn(NO_3)_2$: NaOH = 12:1·24. [e] $HS(CH_2)_2SH$:$Zn(NO_3)_2$:NaOH = 6:1:15.

been able to isolate solid complexes containing thiolate/Hg^{2+} = 4*. Similarly, $(Ph_4P)_2[Hg(SePh)_4]$ has been isolated (together with several related complexes having $PhSe^-/Hg^{2+} < 4$) [25]. Recently, we have shown that the analogous $Cd(SePh)_4^{2-}$ exists in solution [2] and thus we assume that $Zn(SePh)_4^{2-}$ is formed from $Zn(SePh)_2$ and excess $PhSe^-$ also.

NMR Spectra of the Thiolatozincates and $Zn(SePh)_4^{2-}$

A survey of the ^1H and/or ^{13}C NMR spectra of (excess RS^-): Zn^{2+} mixtures in CD_3OD for several representative thiolates showed that ZnS_4 species are the highest formed, that these thiolatozincates are less labile than their cadmium analogs [1], and that the ^1H and/or ^{13}C NMR complexation shifts of the zinc complexes are very like those reported [1] for the corresponding cadmium complexes. For example, (excess $^-S(CH_2)_2S^-$): Zn^{2+} mixtures show separate free and bound ^1H resonances at ambient probe temperature, 306 K, $\Delta\delta_H$ (= $\delta_{H,complex} - \delta_{H,free}$) being 0.04 ppm, integral analysis gives $L_{bound} \cdot Zn^{2+} \approx 2$. For comparison, separate proton resonances of $Cd(^{S}_{S}])^{2-}$ and free $^-S(CH_2)_2S^-$ are observed only at reduced temperature, $\Delta\delta_H$ being 0.06 ppm (ave.) at 193 K. Similarly the proton NMR spectra of $Zn(SMe)_4^{2-}$ and free MeS^- are incompletely collapsed at 306 K, but separate signals for $Cd(SMe)_4^{2-}$ and free MeS^- are observed only at or below *ca.* 250 K; $\Delta\delta_H$ is 0.07 ppm for the zinc complex at 213 K, compared with 0.11 ppm for the cadmium complex at 193 K. The existence of the ZnS_4 kernel in the (excess thiolate). Zn^{2+} mixtures is further demonstrated by a comparison of their ^{13}C NMR spectra with those known for $Cd(SR)_4^{2-}$. Thus, in (excess MeS^-):Zn^{2+} mixtures at 213 K, $\Delta\delta_C$ for the methanethiolatozincate is 2.6 ppm, similar to the 2.1 ppm reported for $Cd(SMe)_4^{2-}$ at 193 K, in (excess PhS^-):Zn^{2+} mixtures at 193 K, $\Delta\delta_{C_1}$ and $\Delta\delta_{C_4}$ for the phenylthiolato–zincate are –2.9 and 0.8 ppm, the corresponding values for $Cd(SPh)_4^{2-}$ being –3.0 and 0.8 ppm at the same temperature. (The free and bound signals of $C_{2,6}$ and $C_{3,5}$ are not resolved for either $Zn(SPh)_4^{2-}$ or $Cd(SPh)_4^{2-}$.) At 308 K $Zn(SPh)_4^{2-}$ exchanges at an intermediate rate the excess free ligand, the free and bound C_1 resonances being incompletely collapsed together. Under the same conditions a sharp single C_1 resonance is observed for (excess PhS^-) Cd^{2+} mixtures, showing that free-bound ligand exchange is fast on the NMR timescale for the cadmium complex. Similarly ligand exchange at 308 K occurs rapidly for (excess tdt^{2-}): Cd^{2+} mixtures, but at an intermediate rate for tdt^{2-}: Zn^{2+} mixtures.

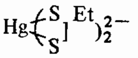
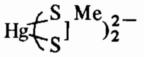
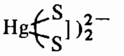
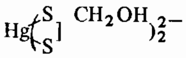
The 297 K 25.04 MHz ^{67}Zn NMR spectra of several typical thiolatozincates in D_2O were measured; the results are summarized in Table I. The resonance of $Zn(SMe)_4^{2-}$ is comparatively sharp, *ca.* 110 Hz in the absence of excess hydroxide; the linewidth increases with increasing concentration of excess OH^-, presumably a viscosity effect, and decreases with increasing temperature, consistent with the rate of quadrupolar relaxation of the ^{67}Zn nucleus (spin, I = 5/2) controlling the linewidth. (Both an increased tumbling rate and an increased rotation rate about the Zn–S bond (leading to a time-averaged symmetry closer to T_d) should cause a decrease in the rate of quadrupolar relaxation and hence a sharper ^{67}Zn resonance). As expected, the linewidths are greater for the complexes of the less symmetric monothiolates and $PhSe^-$ as well as for $Zn(^{S}_{S}])_2^{2-}$.

The variation of the ^{67}Zn NMR chemical shift with ligand, *i.e.* $^-S(CH_2)_2S^- > MeS^- > Pr^iS^- > PhS^- > PhSe^-$, is the same sequence observed for the corresponding cadmium complexes [1, 2]. In other work, the sequence $\delta_{2nd\,row\,donor} > \delta_{3rd\,row\,donor}$ has been observed for the ^{67}Zn resonances of solid ZnS and ZnSe (which contain tetrahedrally coordinated zinc) [27], and calculated from exchange-averaged spectra for ZnX_4^{2-} [28]. The overall range of metal chemical

---

*To complete the isolation of the series $M(SPh)_4^{2-}$ (M = Zn, Cd, or Hg), we have prepared $(Me_4N)_2[Cd(SPh)_4]$ (see Experimental Section) Very lately Dance and coworkers have synthesized salts of $[Cd(SPh)_4]^{2-}$ also [26].

TABLE II Mercury-199 NMR Spectral Parameters of Some Thiolatomercurates and $Hg(SePh)_4^{2-}$.[a]

Complex[b]	$[Hg]_{total}$ (*M*)	δ_{Hg} (ppm)[c]	Approximate $\nu_{1/2}$ (Hz)[b]
$Hg(SMe)_4^{2-}$	0.11	1879[d]	4[d]
$Hg(SEt)_4^{2-}$	0 11	1951	20
$Hg(SPr^i)_4^{2-}$	0.10	1978	36
$Hg(SPh)_4^{2-}$	0 07	1668	75
	0.10	2202	50
	0.13	2191	17
	0.10	2193	24
	0.13	2195	50
$Hg(tdt)_2^{2-}$[f]	0.10	2234	8
$Hg(SePh)_4^{2-}$[g]	0.10	1275	56

[a] 297 K spectra measured at 71.51 MHz using H_2O:D_2O (1:1 (v:v)) solutions containing monothiol (selenol) $Hg(NO_3)_2$ NaOH = 12:1 24 or dithiol: $Hg(NO_3)_2$.NaOH = 6.1:18, except where noted. [b] See text. [c] Relative to 0.1 *M* $Hg(ClO_4)_2$ in 5% (v:v) $HClO_4$, shifts to higher frequency than the reference are taken as positive. [d] With MeSH $Hg(NO_3)_2$ NaOH = 12 1:12 ($[Hg]_{total}$ = 0 11 *M*) at 297 K, δ_{Hg} = 1878 ppm and $\nu_{1/2} \approx$ 18 Hz. [e] PhSH:$Hg(NO_3)_2$·NaOH = 24:1:24. [f] tdt^{2-} = toluene-3,4-dithiolate [g] PhSH:$Hg(NO_3)_2$:NaOH = 10 1:20.

shifts of the thiolatozincates and tetrakis(phenoselenolato) zincate is smaller than found for the corresponding cadmium complexes [1, 2]. A similar situation exists for ZnX_4^{2-} *vs.* CdX_4^{2-} [28–31] and ZnE *vs.* CdE (E = S or Se) [27, 32].

Our ^{67}Zn NMR studies have established the range of chemical shifts to be expected for discrete thiolatozincates. Even with the large ^{67}Zn linewidths it is possible to distinguish readily between free Zn^{2+} (aq) and thiolatozincates. With ^{67}Zn enrichment, direct observation of the bound zinc of Zn–MT might be possible. However, the larger linewidths and smaller expected range of the ^{67}Zn resonances will probably preclude the resolution of separate resonances for closely related binding sites which has been so informative in the ^{113}Cd NMR spectrum of Cd–MT [3c,d].

NMR Spectra of the Thiolatomercurates and Hg(SePh)$_4^{2-}$

We were unable to obtain slow exchange ^{1}H or ^{13}C NMR spectra of any (excess thiolate) Hg^{2+} mixture tried, or of (excess $PhSe^-$).Hg^{2+} mixtures, at any temperature in methanol as solvent. However, as discussed above, the presence of the HgS_4 complexes and $Hg(SePh)_4^{2-}$ in the appropriate mixtures may be inferred from the isolation of representative species in the solid state. Further, as the existence in solution of tetrathiolatozincates has been demonstrated above, and of tetrathiolatocadmates and Cd(SePh)$_4^{2-}$ previously [1, 2], this inference is supported by the parallel chemical behaviour found for the systems Zn^{2+}–, Cd^{2+}–, and Hg^{2+}–thiolate (or $PhSe^-$). It is clear that in the tetrathiolatometallates of Group IIB the order of lability is $Hg^{2+} > Cd^{2+} > Zn^{2+}$. The order $Hg^{2+} > Cd^{2+}$ has been found earlier for MX_4^{2-} [30] (though it should be noted that excess ligand was not present in this study) and $Cd^{2+} > Zn^{2+}$ is observed in various complexes of the type $M(EPR_3)_4^{2+}$ (E = S or Se) [33].

The results of 71.5 MHz ^{199}Hg NMR measurements on various thiolatomercurates and $Hg(SePh)_4^{2-}$ are presented in Table II. At 297 K, in H_2O/D_2O as solvent, all the complexes studied gave reasonably sharp ^{199}Hg resonances. The linewidths given in Table II are probably best regarded as upper limits, as the temperature coefficients of the chemical shifts appear to be substantial, so appreciable linewidth contributions from slight temperature gradients within the samples are possible. The chemical shifts are however reproducible.

The pattern of ^{199}Hg chemical shifts of the various mercury (II) complexes shows the same gross features as the metal NMR of the zinc and cadmium analogs, *i.e.* $^-S(CH_2)_2S^- > RS^-$ (R = alkyl) $> PhS^- > PhSe^-$ although, as expected (*e.g.* Refs 28–31), the overall range of the ^{199}Hg chemical shifts is larger than found for the other two metals. However the effect of alkyl substitution on the backbone of $^-S(CH_2)_2S^-$ (in the complexes of 1,2-propane- and 1,2-butane-dithiolates) is smaller than found for the corresponding cadmium complexes. Also, the deshielding effect of increasing methyl substitution in complexes of $Me_{3-n}H_nCS^-$ is the reverse of the trend found for the parallel zinc and cadmium complexes. The deshielding effect associated with five-membered chelate ring formation (as measured, for instance, by $\delta(\mathrm{M}(\overset{S}{\underset{S}{\langle}}])_2^{2-}) < \delta(\mathrm{M}(SMe)_4^{2-}))$ varies with metal in the sequence Hg > Cd > Zn. The small range observed for the ^{199}Hg NMR chemical shifts of the complexes of $^-SCH_2CHRS^-$ (R = H, Me, Et or CH_2-OH) and tdt^{2-} makes it clear that all these ligands coordinate to mercury in a like manner, presumably as bidentate chelating dithiolates, at the high pH's used for our studies. The shielding sequence $\delta_{\mathrm{2nd\,row\,donor}} > \delta_{\mathrm{3rd\,row\,donor}}$, found here for the resonances of $Hg(EPh)_4^{2-}$ (E = S or Se) has commonly been observed for the Group IIB elements (*e.g.*, see above and Refs. 2, 27–32, 34). Fortunately the shift observed for $Hg(SePh)_4^{2-}$ is well outside the range found for the thiolatomercurates, suggesting that δ_{Hg} may be usable as an indicator of Hg–Se bond formation. This tentative conclusion would be strengthened by the study of mercury complexes of a wider range of selenolates.

Attempts to obtain separate ^{199}Hg resonances for mixed ligand species in ternary mixtures of the type $R'S^-$–RS^-–Hg^{2+} in CD_3OD at reduced temperature (and so confirm the MS_4 stoichiometry as was successfully done for the cadmium complexes [1]) yielded very broad lines. This result must reflect the high lability of the mercury complexes, which may be the main barrier to measurement of well resolved ^{199}Hg NMR spectra of mercury thioneins.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) fo support of this research under the Strategic Grants Program (Environmental Toxicology). The high-field NMR data were obtained at the Southwestern Ontario NMR Centre funded by a major installation grant from NSERC. We thank Mr. Bruce MacDonald of the S.W. Ontario NMR Centre and Mrs. Heather Schroeder of this Department for expert technical assistance in obtaining various NMR spectra, Drs. J. S. Hartman of Brock University and M. J. Stillman of this Department for helpful discussions.

References

1 G. K. Carson, P. A. W. Dean and M. J. Stillman, *Inorg. Chim. Acta, 56,* 59 (1981).
2 G. K. Carson and P. A. W. Dean, *Inorg. Chim. Acta, 66,* 37 (1982).
3 a) J. D. Otvos and I. M. Armitage, Abstr. Symp. on Metallothioneins and Other Low Molecular Weight Metal-Binding Proteins, Zurich, Switzerland, July 1978;
b) I. M. Armitage, J. D. Otvos, J. F. Chlebowski and J. E. Coleman, Abstr. 20th Exptl. NMR Conf., Asilomar, California, Feb. 1979;
c) J. D. Otvos and I. M. Armitage, *J. Am. Chem. Soc*, *101,* 7734 (1979);
d) J. D. Otvos and I. M. Armitage, *Proc. Natl. Acad. Sci. U.S.A., 77,* 7094 (1980).
4 P. J. Sadler, A. Bakka and P. J. Beynon, *FEBS Lett , 94,* 315 (1978).
5 K. T. Suzuki and T. Maitani, *Experientia, 34,* 1449 (1978).
6 R. Olafson and J. D. Otvos, private communication.
7 T. A. Gasiewicz and J. C. Smith, *Environ. Health Perspectives, 25,* 133 (1978), and refs. therein.
8 J. Parízek, I. Benes, I. Ostádalová, A. Babický, J. Benes and J. Pitha, in 'Mineral Metabolism in Pediatrics', D. Parltrop and W. L. Burland eds., F. A. Davis, Philadelphia, 1969. Ch 8 and refs. therein.
9 H. E. Ganther, in 'Selenium', R. A. Zingaro and W. C. Cooper eds., Van Nostrand Reinhold, New York, 1974. Ch. 9 and refs. therein.
10 E. J. Underwood, 'Trace Elements in Human and Animal Nutrition', 4th edn., Academic Press, New York, 1977.
a) Ch. 9 and 12 and refs. therein;
b) Ch. 12 and 14 and refs. therein.
11 J. H. R. Kägi and B. L. Vallee, *J. Biol. Chem., 235,* 3460 (1960).
12 D. R. Winge, R. Premakumar and K. V. Rajagopalan, *Arch. Biochem Biophys., 170,* 242 (1975).
13 A. P. Leber and T. S. Miya, *Toxicol. Appl. Pharmacol*, *37,* 403 (1976).
14 L. Magos and M. Webb, *Top. Environ. Health, 3,* 581 (1979), and refs. therein.
15 I. G. Dance, *J. Am Chem. Soc., 101,* 6264 (1979).
16 D. C. Bradley and C. H. Marsh, *Chem. and Ind (London),* 361 (1967).
17 A. J. Canty, R. Kishimoto, G. B Deacon and G. J. Farquharson, Inorg. Chim. Acta, 20, 161 (1976).
18 M. E. Peach, *J. Inorg. Nuclear Chem., 41,* 1390 (1979)
19 A. J. Carty and S. F. Malone, *Top Environ Health, 3,* 445 (1979), and refs. therein.
20 D. Spinelli and C. Dell'Erba, *Ann. Chim., 51,* 45 (1961); *Chem. Abstr*, *55,* 14351b (1961).
21 Y. Okamoto and T. Yano, *J Organometal. Chem., 29,* 99 (1971).
22 I. G. Dance, (a) *Inorg. Chem., 20,* 2155 (1981); (b) *J. Am. Chem. Soc., 102,* 3445 (1980); (c) *J. Chem. Soc. Chem. Comm.,* 818 (1980), (d) Abstr. 179th A.C.S. Natl. Meeting, Houston, Texas, March 1980, Abstr INOR 42.
23 D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc., 97,* 6917 (1975).
24 D. Coucouvanis, private communication.
25 J. Liesk and G. Klar, *Z. Anorg. Chem., 435,* 103 (1977).
26 I G. Dance, P. J. Guerney and W. Zimmerman, unpublished work quoted in Ref. 21a.
27 M. Haller, W. E. Hertler, O. Lutz and A. Nolle, *Solid State Comm., 33,* 1051 (1980).
28 G. E. Maciel, L. Simeral and J. J. H. Ackerman, *J. Phys. Chem*, *81,* 263 (1977).
29 J. J. H. Ackerman, T. V. Orr, V. J. Bartuska and G. E. Maciel, *J. Am. Chem. Soc., 101,* 341 (1979).
30 R. Colton and D. Dakternieks, *Aust. J. Chem., 33,* 2405 (1980).
31 R. S. Honkonen and E. L. Amma, Abstr. 181st A.C.S. Natl. Meeting, Atlanta, Georgia, March 1981, Abstr. INOR 144.
32 A. Nolle, *Z Naturforsch*, *33a,* 666 (1978).
33 G. K. Carson and P. A. W. Dean, unpublished results.
34 P. A. W. Dean, *Can. J. Chem., 59,* 3221 (1982).