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Spectroscopic Characterization of Anionic Tris(*N*,*N*-dialkyldithiocarbamate) Complexes of Zinc(II) and Cadmium(II)

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Abstract

The infrared and Raman spectra (1500–50 cm^{-1}) of the related complexes $Zn(S_2CNMe_2)_2$ (**I**), $[Bu_4N][Zn(S_2CNMe_2)_3]$ (**II**), $Cd(S_2CNMe_2)_2$ (**III**), $[Bu_4N][Cd(S_2CNMe_2)_3]$(**IV**), $Cd(S_2CNEt_2)_2$ (**V**) and $[Bu_4N][Cd(S_2CNEt_2)_3]$ (**VI**) have been determined. For complexes with coordination number four, metal–sulfur stretching frequencies were assigned at 228 cm^{-1} for **I** (Zn–S), 180 cm^{-1} for **III** (Cd–S) and 208 cm^{-1} for **V** (Cd–S), whereas for complexes with apparent coordination number six they were assigned at 206 cm^{-1} for **II** (Zn–S) and in the 150–125 cm^{-1} range for **IV** and **VI** (Cd–S). Thus, expansion of the coordination sphere of the Zn(II) and Cd(II) metal results in a significant shift towards lower energy of the far IR M–S vibrations. Other M–S sensitive vibrations in the far IR are found in the 385–350 cm^{-1} range, and are described as mixed ring bending modes with significant M–S stretching contribution.

Introduction

The chemistry and structural characteristics of neutral bis(*N*,*N*-dialkyldithiocarbamate) complexes $M(S_2CNR_2)_2$ with M = Zn(II) or Cd(II) have been extensively reviewed [1, 2]. McCleverty *et al.* [3–5] have studied the tendency of the Zn(II) and Cd(II) ions to expand further their coordination number by interaction with additional $S_2CNR_2^-$ ligand units to form binary anionic adducts which are of significance in relation to the inorganic aspects of rubber vulcanization. In particular, the $Zn(S_2CNMe_2)_3^-$ and $Cd(S_2CNEt_2)_3^-$ complexes have been isolated as Bu_4N^+ salts and well characterized. A single crystal X-ray structure of the $Zn(S_2CNMe_2)_3^-$ anion shows one chelate dithiocarbamate ligand and two nearly monodentate ligands in a distorted tetrahedral coordination geometry [4], whereas the structure of the $Cd(S_2CNEt_2)_3^-$ complex shows that the Cd atom is six coordinate with a geometry which is intermediate between trigonal prismatic and octahedral with a slight asymmetry in the chelation of each diethyldithiocarbamate ligand [5].

The tris(*O*-ethylxanthate) Cd(II) complex anion $Cd(S_2COEt)_3^-$, where the S_2COEt^- ion is also a potentially chelating ligand, has been shown by X-ray analysis to contain a five coordinate Cd central atom, with two bidentate ligands and a third xanthate ion acting as a truly monodentate ligand [6].

The present work was undertaken in order to extend the available information on the Zn(II)– and Cd(II)–sulfur coordination units in binary dithiocarbamate complexes and to ascertain wether it is possible to associate well defined frequency regions to the different coordination units in these complexes. The IR and Raman spectra (1500–50 cm^{-1}) of $Cd(S_2CNR_2)_2$ and $Cd(S_2CNR_2)_3^-$ (R = Me, Et) together with those of $Zn(S_2CNMe_2)_2$ and $Zn(S_2CNMe_2)_3^-$ complexes are here assigned and discussed.

Experimental

Physical Measurements

Microanalyses and ^1H NMR spectra in $DCCl_3$ solution at 100 MHz using a Varian HA100 were performed at UMYMFOR. Zn and Cd analyses by atomic spectrophotometry were performed at the Analytical Division of the DQIAyQF. Infrared spectra were recorded in the 400–350 cm^{-1} range with a Beckman 4260 grating spectrophotometer and in the 400–40 cm^{-1} range with a Fourier Digilab FTS-18C. Frequency readings were calibrated with polystyrene film and water vapor. The samples were studied as Nujol and Halocarbon mulls supported between CsI and polyethylene disks. KBr pellets were also run and no significant differences were

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observed. Raman spectra of pressed powdered solids were obtained from a Jarrel Ash 25-300 spectrophotometer equipped with a Coherent Radiation 52G argon ion laser. The laser power of the 5145 A excitation line measured at the solid sampels was *c.* 100 mW. The scattered radiation was observed at 90° to the incident beam and the spectral slit width was conveniently adjusted at different frequency ranges.

Preparation of Compounds

Zn(S$_2$CNMe$_2$)$_2$, Cd(S$_2$CNMe$_2$)$_2$ and Cd(S$_2$CNEt$_2$)$_2$ were prepared by reaction between the sodium salt of the *N,N*-dialkyldithiocarbamate ligand and the corresponding metal(II) chloride in water [1, 2]. The solid complexes $M(S_2CNR_2)_2$ (M = Zn, R = Me; M = Cd, R = Me, Et) precipitated immediately and were filtered hot to remove the NaCl and any excess unreacted NaS_2CNR_2. The solids were dried *in vacuo* at 80 °C. $Zn(S_2CNMe_2)_2$ and $Cd(S_2CNEt_2)_2$ were recrystallized from boiling benzene and $Cd(S_2CNMe_2)_2$ was used as obtained since it proved too insoluble in common organic solvents to be recrystallized.

[Bu$_4$N][S$_2$CNMe$_2$] in acetone solution was prepared by addition of $[Bu_4N]Cl$ (5.56 g, 0.02 mol) in acetone (100 ml) to NaS_2CNMe_2 (3.58 g, 0.02 mol) in acetone (100 ml). The mixture was cooled to about 0 °C and the NaCl formed was removed by filtration. The filtrate was condensed to approximately 100 ml in a rotary evaporator and used in this form in the following preparations.

[Bu$_4$N][S$_2$CNEt$_2$] was prepared in a similar way.

[Bu$_4$N][Zn(S$_2$CNMe$_2$)$_3$]. This compound was prepared by the method described by McCleverty and Morrison [3] and was analyzed to ensure identification.

The cadmium complexes $[Bu_4N][Cd(S_2CNR_2)_3]$ (R = Me, Et) were prepared as described by McCleverty *et al.* [5] with slight modifications.

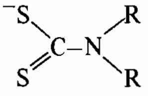
[Bu$_4$N][Cd(S$_2$CNMe$_2$)$_3$]. To a solution of $[Bu_4N][S_2CNMe_2]$ (5.1 g, 0.01 mol) in acetone (100 ml) at room temperature was added powdered solid $Cd(S_2CNMe_2)_2$ (4.0 g, 0.01 mol) in small portions. The mixture was well stirred until all the solid had dissolved (*c.* 24 h) and then was filtered to remove any unreacted $Cd(S_2CNMe_2)_2$. Petrol ether (50 ml) was added slowly and the total volume of the solution was reduced to 80 ml in a rotary evaporator, filtered and then allowed to stand at 0 °C while the product crystallized as colorless needles in a period of two days. Recrystallization was from petrol ether and acetone in 1:1 ratio at room temperature (yield 70%). *Anal.* Calc. for $C_{25}H_{54}N_4S_6Cd$: C, 41.96; H, 7.61; N, 7.83; S, 26.89; Cd, 15.71. Found: C, 42.15; H, 7.42; N, 7.62; S, 26.63; Cd, 15.13%.

[Bu$_4$N][Cd(S$_2$CNEt$_2$)$_3$]. To a solution of $[Bu_4N][S_2CNEt_2]$ (5.4 g, 0.01 mol) in acetone (100 ml) at room temperature was added powdered solid $Cd(S_2CNEt_2)_2$ (4.1 g, 0.01 mol) in one portion. The mixture was stirred only until all solid had dissolved (*c.* 15 min) and then filtered to remove any unreacted $Cd(S_2CNEt_2)_2$. The solution was then allowed to stand at 0 °C while the product crystallized as colorless crystals overnight. Recrystallization was from acetone at room temperature (yield 75%). *Anal.* Calc. for $C_{31}H_{66}N_4S_6Cd$: C, 46.59; H, 8.27; N, 7.01; S, 24.05; Cd, 14.08. Found: C, 46.74; H, 7.98; N, 6.97; S, 24.42; Cd, 14.68%. ^1H NMR $DCCl_3$: 0.96 (t, $N(CH_2CH_2CH_2\mathit{CH_3})_4$); 1.24 (t, $N(CH_2\mathit{CH_3})_2$); 1.50 (m, $N(CH_2\mathit{CH_2CH_2}Me)_4$); 3.26 (t, $N(\mathit{CH_2}Prn)_4$); 3.92 (q, $N(\mathit{CH_2}Me)_2$).

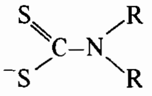
Results and Discussion

The IR and Raman vibrational frequencies for the metal(II) dithiocarbamate complexes $Zn(S_2CNMe_2)_2$, $[Bu_4N][Zn(S_2CNMe_2)_3]$, $Cd(S_2CNMe_2)_2$ and $[Bu_4N][Cd(S_2CNMe_2)_3]$ are given in Table 1. The frequency regions reported as sensitive to the nature of the metal to ligand coordination in the IR spectra are those at 1550–1450, 1050–950 and 400–350 cm^{-1} and that have been assigned to ν(C–N), ν(C–S) and ν(M–S) vibrations respectively [7] will be now discussed.

All complexes in Table 1 exhibit strong bands in the 1540–1470 cm^{-1} region, the 'thioureide' band due primarily to the ν(C–N) vibrations of the ligands. For the $M(S_2CNMe_2)_2$ complexes M = Zn or Cd, the bands are centered at around 1520 cm^{-1} and undergo downward shifts to 1485 cm^{-1} by anionic complex formation which is close to the corresponding ν(C–N) value of the ionic salt NaS_2CNMe_2. The downward frequency shifts observed suggest that canonical form 1c contributes less to the overall structure in the anionic complex ligands than it does in the parent dialkyldithiocarbamates. No further details are observed in either the IR or Raman spectra in this region, due to the broad nature of the ν(C–N) band in these complexes. The relatively large shifts in ν(C–N) as a result of adduct formation, appear to be quite general and have been reported for adduct complexes with S, N or O as the ligand donor atoms [2, 5, 8].



1a



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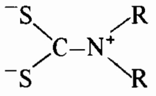

1c

The frequencies in the 1050–950 cm^{-1} range are associated with the prevailing contribution of ν(C–S). Absorptions at 978 (IR), 976 (Raman) and 962

TABLE 1. Infrared and Raman frequencies (cm^{-1}) of $Zn(S_2CNMe_2)_2$ (I), $[Bu_4N][Zn(S_2CNMe_2)_3]$ (II), $Cd(S_2CNMe_2)_2$ (III) and $[Bu_4N][Cd(S_2CNMe_2)_3]$ (IV)[a, b, c]

I		II		III		IV		Assignment
IR	R	IR	R	IR	R	IR	R	
1530s								
1520s				1520s	1520w			ν(CN)
	1512s							
		1480s	1484m			1490s		
						1480sh		
1245s	1241w	1250s		1246s	1240w	1256s		ν(NMe)
		990s	986w			982s	984sh	ν(CS)
978s	976m	972s	976m			970s	968m	
	962m		968w	968sh				
				959s	950s			
570m	568s	576m	573s	569m	572s	575m	572s	ν(CS) + δ(SCS)
448m		448m		449s		449s		δ(CNC')
440sh		440sh		440sh		440sh		
	434s		433s		434s		432m	
383s								
		372w						ν(M–S) + δ(SCN) + δ(SCS)
363sh	367w	362sh	374w	363s	358w	359s	360w	
		340w	342w					
228s	220w	206s	211w					ν(Zn–S)
				183m	180s			ν(Cd–S)
177m				173m				ν(M–S) + δ(MSC)
170m	168s			165m				
					142s	147s	147w	ν(Cd–S)
				135m		140s		
							125m	
120m		128m						
100m			113m	103m		115s		
				95m	90s			
							88m	
60w		60m	78m	67m	57s	57m		
				32m		44m		

[a] s, m, w and sh refer to strong, medium, weak and shoulder, respectively. [b] The CH_3 deformation modes, asymmetric and symmetric, and the CH_3 rocking modes which occur at frequencies around 1445 and 1400 in the former and at 1148 and 1050 cm^{-1} in the latter are not included in this Table. [c] For comparison purposes, selected IR and Raman frequencies of the NaS_2CNMe_2 salt are given (Raman values in brackets): 1490s (1495m), 1245s, 967s (966w), 570w (568s), 540m, 485w, 451 (438s), 333s (332w), 200m (192m), (142m), 120m, 100m (92vs), (78vs) and (54vs).

(Raman) cm^{-1} in $Zn(S_2CNMe_2)_2$ remain comparatively invariant in the $Zn(S_2CNMe_2)_3^-$ complex anion which shows, in addition, a new strong IR band at 990 cm^{-1} and a weak Raman line at 986 cm^{-1}. A split in the IR at around 1000 cm^{-1} has been taken as indicative of the inequivalence of the C–S bonds in the monodentate dithiocarbamate coordination [9], and on this bases the two IR bands in $Zn(S_2CNMe_2)_3^-$ can be attributed to the simultaneous presence of bidentate and monodentate groups.

Normal coordinate analysis calculations have shown that unsymmetrical bidentate bonding of dithiocarbamates produces splitting effects on the ν(C–N) band at around 1500 cm^{-1} and on the ν(C–S) band at around 1000 cm^{-1} and that the extent of splitting increases as the bonding becomes more unsymmetrical [7]. The suggestion has been made that only if the splitting in the 1000 cm^{-1} region is greater then 20 cm^{-1} should truly monodentate coordination be assumed. The chelate $Zn(S_2CNMe_2)_2$ complex [10] exhibits only one strong IR band at 978 cm^{-1} whereas $Zn(S_2CNMe_2)_3^-$ exhibits two strong IR bands at 972 and 990 cm^{-1} with a splitting of 18 cm^{-1}. Inspection of Table 1 shows that the frequencies of the Raman lines around 1000 cm^{-1} exhibit a similar pattern to that observed

TABLE 2. Selected infrared and Raman frequencies (cm^{-1}) of $Cd(S_2CNEt_2)_2$ (V) and $[Bu_4N][Cd(S_2CNEt_2)_3$ (VI)

V		VI		Assignment
IR	R	IR	R	
994s	992m	998s	1002m	ν(CS)
	980s	986sh	986m	
380s	372w			
375sh				
		366m	368w	ν(CdS) + δ(SCS) + δ(SCN)
		354m		
332m				
		323m	316w	
193s	208s	190w		ν(Cd–S)
			168w	ν(Cd–S) + δ(SCdS)
150w	152m	150s		
100s	108m	100s		
	90s		85s	

in IR for $Zn(S_2CNMe_2)_2$ and $Zn(S_2CNMe_2)_3^-$, thus providing an alternative vibrational criterion for differentiating monodentate from bidentate dithiocarbamate ligands.

The $Cd(S_2CNMe_2)_2$ IR spectrum exhibits a strong band at 959 cm^{-1} (950, Raman) which by adduct formation shows an increase and splitting to a strong doublet at 970 and 982 cm^{-1} and two Raman medium intensity lines at 968 and 984 cm^{-1} respectively. Selected IR and Raman data for the related cadmium ethyl derivative complexes are given in Table 2. In $Cd(S_2CNEt_2)_2$ the strong IR band at 994 cm^{-1} (992 and 980, Raman) is only slightly shifted in $Cd(S_2CNEt_2)_3^-$ to 998 cm^{-1} (986 and 1002, Raman). The splitting in both cases is too small for monodentate coordination of the ligands to be assumed. On the basis of the vibrational criteria reported above, unsymmetrical bidentate coordination may be attributed to the dithiocarbamate molecules in the anionic complexes $Cd(S_2CNMe_2)_3^-$ and $Cd(S_2CNEt_2)_3^-$ suggesting a pseudo-octahedral coordination geometry of the Cd(II) ion. X-ray analysis of complex $Cd(S_2CNEt_2)_3^-$ [5] showed a slight asymmetry in the bidentate bonding of the three ligands in accordance with the conclusion reached by vibrational methods. These results are clearly different from those arrived at for the $Zn(S_2CNMe_2)_3^-$ complex, where monodentate and bidentate dithiocarbamate ligands are present simultaneously in a distorted tetrahedral coordination. The different coordination numbers of the central ions in the anionic complexes may be ascribed to the different radii of the Zn and Cd atoms.

In the 600 to 430 cm^{-1} range three medium IR bands at approximately 570, 448 and 440 cm^{-1} and two strong Raman lines at 570 and 434 cm^{-1} remain practically invariant for all the complexes reported in Tables 1 and 2 including the sodium salts of the ligands and are therefore ascribed to the vibrational modes of the ligand part of the molecule.

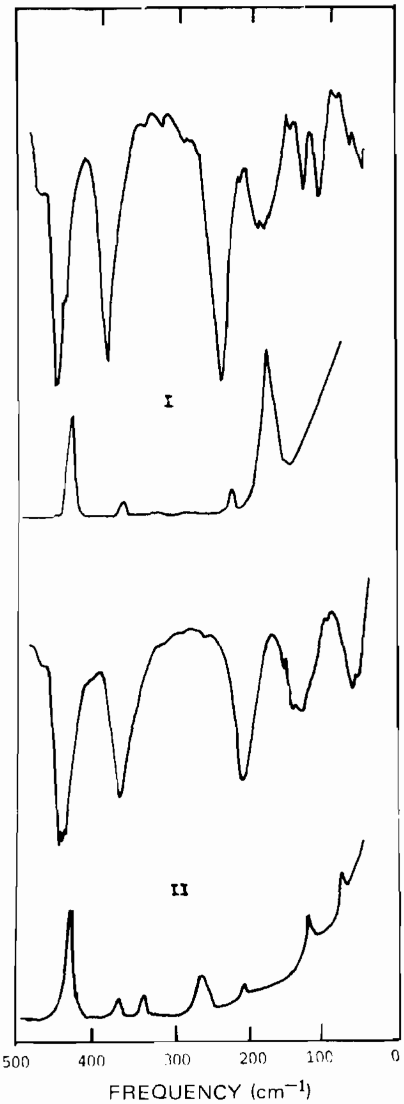

Fig. 1. Far-infrared and Raman spectra (500–40 cm^{-1} region) of $Zn(S_2CNMe_2)_2$ (I) and $[Bu_4N][Zn(S_2CNMe_2)_3]$ (II) in the solid state.

The spectra in the low frequency region (400 cm^{-1}) in Figs. 1–3 are strongly dependent on the M–S structural units and on the identity of the metal. Mixing of the normal vibrations that fall together in this narrow range of the spectrum are likely to occur and the assignments of these frequencies to the vibrational modes given in Tables 1 and 2 must be regarded as crude approximations.

The first new vibrations found below 400 cm^{-1} in the spectra of $Zn(S_2CNMe_2)_2$ and $Cd(S_2CNMe_2)_2$ chelate complexes are the IR bands at 383 and 363 (367 and 358 Raman) cm^{-1} respectively. By adduct

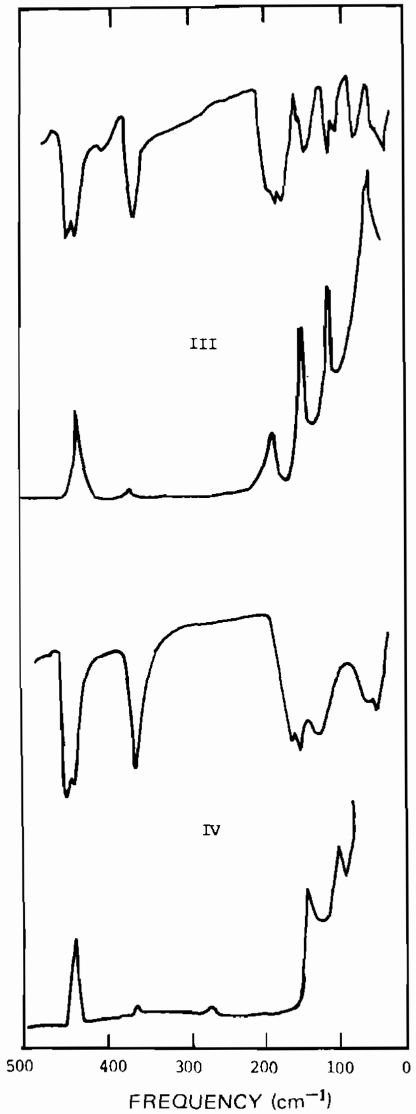

Fig. 2. Far-infrared and Raman spectra (500–40 cm^{-1} region) of $Cd(S_2CNMe_2)_2$ (III) and $[Bu_4N][Cd(S_2CNMe_2)_3]$ (IV) in the solid state.

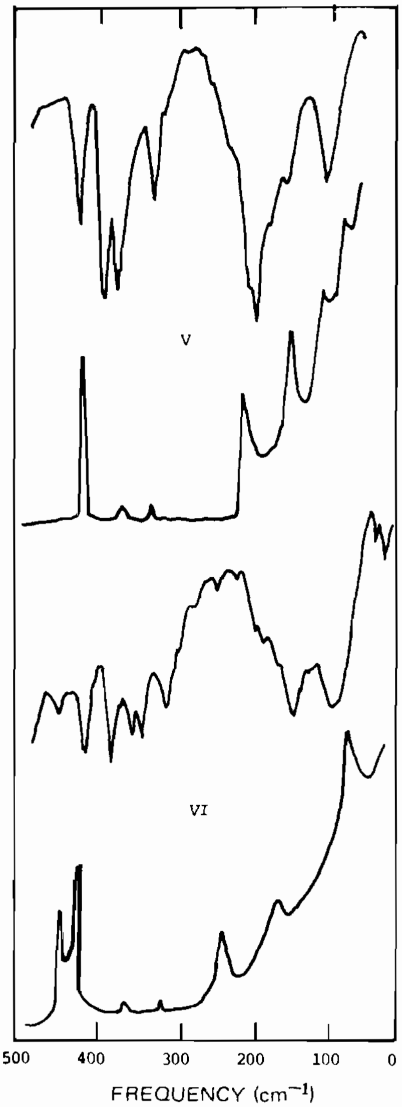

Fig. 3. Far-infrared and Raman spectra (500–40 cm^{-1} region) of $Cd(S_2CNEt_2)_2$ (V) and $[Bu_4N][Cd(S_2CNEt_2)_3$ (VI) in the solid state.

formation these frequencies undergo downward shifts to 372 (374 Raman) for $Zn(S_2CNMe_2)_3^-$ and to 359 (352 Raman) cm^{-1} for $Cd(S_2CNMe_2)_3^-$. The nearest absorption band of the $S_2CNMe_2^-$ ligand is the IR band at 330 (332 Raman) cm^{-1} which we assign to a SCN or SCS bending mode by analogy to the assignation proposed for the ethyl derivative [11]. This ligand mode appears as strongly affected by coordination to a metal center, and moves to higher frequencies in the 400–350 cm^{-1} range to a value which is dependent on the nature of the metal. The M–S contribution to these modes is apparent by the 10 to 20 cm^{-1} shifts to lower frequencies of the cadmium vibrational modes with respect to those of the zinc homologues, as observed for M–SPh vibrations of terminal ligands [12]. So, it seems reasonable to assign the bands at 383 and 363 and at 372 and 359 cm^{-1} to ring deformation modes of $M(S_2CNMe_2)_2$ and $M(S_2CNMe_2)_3^-$ (M = Zn, Cd) respectively, with significant contributions from M–S stretching modes. In addition, a weak IR band at 340 (342 Raman) cm^{-1} accompanies the 372 cm^{-1} vibration in the spectrum of $Zn(S_2CNMe_2)_3^-$ and can be taken as indicative of the inequivalence of the M–S bonds when both monodentate and bidentate ligand attachment are simultaneously present. The validity of this criterion of the number of bands in the 400–300 cm^{-1} range to determine the nature of the coordination of the dithiocarbamate ligand to the metal, will require systematic studies of other metal dithiocarbamate complexes with different types of ligand bonding. The assignment of these bands is supported by the normal coordinate analysis for $Cr(S_2CNMe_2)_3^-$ where a band at 373 cm^{-1} has been assigned to a ν(Cr–S) + δ(SCN) mode and a shift to 317 cm^{-1} has been calculated for a monodentate coordination in a 1:1 planar model of $Cr(S_2CNMe_2)$ [9]. New IR bands in the region 385–320 cm^{-1} have also been reported for Ni(II) [13, 14], Sn(II) [15] and Pb(II) [16] dithiocarbamate complexes.

Below 250 cm^{-1} the low frequency vibrational spectra of $Zn(S_2CNMe_2)_2$ and $Zn(S_2CNMe_2)_3^-$ exhibit a new strong band at 228 and 206 cm^{-1} and weak Raman counterparts at 220 and 211 cm^{-1} respectively, Fig. 1. We assign the bands at 228 cm^{-1} (220 Raman) and at 206 cm^{-1} (211 Raman) to the Zn–S stretching vibration in the tetrahedral structure and in the distorted tetrahedral structure of the ZnS_4 core of $Zn(S_2CNMe_2)_2$ and $Zn(S_2CNMe_2)_3^-$, respectively. The diminished frequency in the anionic complex indicates weaker Zn–S bond interaction when a third dithiocarbamate ligand enters the coordination sphere of the metal. In fact, X-ray structure determination [4] shows a lengthening of the mean Zn–S bond value (2.375 Å for a ZnS_4 and 2.627 Å for a ZnS_6 core) compared to the mean value of 2.361 Å in the bis-chelate complex [10]. In the IR spectra of the last complex a broad band centered at 174 cm^{-1} with a strong Raman counterpart at 168 cm^{-1} is found, which owing to the position and intensity may be assigned largely to MSC ring deformation modes.

In the spectra of the cadmium complexes the ν(Cd–S) vibrations have dropped below 200 cm^{-1} where various deformation modes with small energy separations are expected, and form together broad and intense bands which cannot be adequately resolved, Figs. 2 and 3. The assignment proposed in Tables 1 and 2 is based primarily on the presence of strong Raman lines at 180 and 142 cm^{-1} for $Cd(S_2CNMe_2)_2$, at 208 and 152 cm^{-1} for $Cd(S_2CNEt_2)_2$ and at 125 cm^{-1} for the $Cd(S_2CNMe_2)_3^-$ complex anion. The Raman spectrum of $Cd(S_2CNEt_2)_3^-$ shows no prominent features below 400 cm^{-1} and the IR spectrum shows a broad absorption band in the 200–140 cm^{-1} range with a maxima centered at 150 cm^{-1}. These results show that the Cd–S absorption bands in the anionic complexes are significantly lower than those in the bis-chelate complexes, and that the magnitude of the shift is about three times that observed for the zinc complexes. These large shifts may result from significantly longer Cd–S bond distances in pseudo-octahedral coordination structures than those reported in the X-ray structural study of the $Cd(S_2CNEt_2)_3^-$ anion [5], where the average Cd–S bond distance is 2.711 Å compared with the average value of 2.57 Å in the essentially tetrahedral $Cd(S_2CNEt_2)_2$ dimer complex [17].

The IR and Raman results reported here in the low frequency region where the spectra are dependent on the metal–sulfur structure type, should be of value in confirming Zn–S and Cd–S binding in similar structural units. Our assignments are consistent with those made for other related systems. For tetrahedral thiourea complexes ν(Zn–S) falls in the range 267–225 cm^{-1} and ν(Cd–S) in the range 237–203 cm^{-1} [18]. In bis-monothioacetylacetonate complexes, Zn–S and Cd–S vibrations have been assigned at 273 and 197 and at 245 and 180 cm^{-1}, respectively [20]. The closest comparison is with a series of Cd(II) chelate complexes with CdS_4 and CdS_5 units reported by Haberkorn *et al.* [21] where the bands in the 220–144 cm^{-1} interval have been assigned to Cd–S stretching vibrations.

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