Vibrational spectra and structure of cadmium(II) thiocyanate

R. G. GOEL

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario,

Canada N1G 2W1

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Abstract—Infrared and Raman spectral data (4000-50 cm⁻¹) of cadmium(II) thiocyanate are consistent with a polymeric structure having a centro-symmetric octahedral coordination polyhedron around cadmium.

Infrared frequencies [1, 2] due to the internal vibrations of the thiocvanate group have been widely used to determine the mode of bonding of the thiocyanate ligand in metal thiocyanates and their complexes containing other ligands. Various spectroscopic criteria [1, 2] correlating the CN and CS stretching and SCN bending frequencies with the mode of bonding of the thiocvanate group have been proposed and reviewed. Despite the wide practice of using infrared criteria to determine the mode of bonding of the thiocyanate ligand, little attention has been given to test the validity of these criteria by studying the spectra of compounds of known structures. Furthermore, the spectra in the far i.r. region where the vibrations involving metal-ligand bonds are expected to occur have remained virtually unexplored. Raman spectral studies on metal thiocyanates have also been lacking.

Infrared and Raman spectra[3] of cadmium(II) thiocyanate complex of tri-*tert*-butylphosphine were examined recently in this laboratory. Soon after this study, the crystal structure of cadmium(II) thiocyanate was reported [4]. Its i.r. and Raman spectra in the 4000–50 cm⁻¹ are reported herein.

The crystal structure data show that cadmium(II) thiocyanate has a polymeric structure in which each thiocyanate group is bonded to three cadmium atoms in such a manner that each cadmium is octahedrally coordinated to four sulphur and two nitrogen atoms which are *trans* to each other. The Cd-N bonds are stronger than Cd-S bonds. The equatorial Cd-S bonds are also stronger than the axial Cd-S bonds.

The observed infrared and Raman frequencies for cadmium(II) thiocyanate, in the solid state, in the 4000-50 cm⁻¹ region are listed in Table 1. As shown by the data in Table 1 three infrared and two Raman frequencies are observed in the CN stretching as well as the SCN bending regions. In the CS stretching region only a weak band is observed in the i.r. as well as in the Raman; the weak i.r. band at 900 cm⁻¹ can be assigned as an overtone of the SCN bending frequency at 450 cm⁻¹. The observed CN and CS stretching and the NCS bending frequencies for cadmium(II) thiocyanate are thus in the ranges suggested [1, 2] for the bridging thiocyanate, M-NCS-M. The vibrational frequencies of the thiocyanate group, therefore, do not provide any differentiation between bidentately, and tridentately bridging thiocyanates.

The remaining infrared and Raman bands in Table 1 are attributable to the skeletal and/or lattice vibrations. The skeletal stretching frequencies can be assigned unequivocally on the basis of the structural information provided by the crystallographic data. The skeletal symmetry of the coordination polyhedron around each cadmium can be approximately described as D_{4h} and the application of group theory leads to the following fundamental vibrations:

$$2A_{1g} + 2A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3E_u$$

of these, the vibrations belonging to the species A_{1e} , B_{1g} , B_{2g} and E_g are only Raman active, and those of A_{2u} and E_u are only infrared active. The two Cd-N bonds will give rise to two Cd-N stretching frequencies belonging to the A_{1g} and A_{2u} species, and the four Cd-S bonds will give rise to three Cd-S stretching frequencies belonging to the A_{1g} , B_{1g} and E_{u} species. The remaining vibrations are due to the bending modes. The Cd-N stretching frequencies are expected to be higher than the Cd-S stretching frequencies. The assignments for the Cd-N and Cd-S stretching frequencies shown in Table 1 follow in a straight forward manner from the aforementioned considerations. The proposed assignments for the Cd-N stretching frequencies are consistent with the Cd-N stretching frequencies reported for the octahedral cadmium(II) halide complexes of pyridine type ligands [5] and the cationic octahedral complexes of nitrile ligands [6]. Unfortunately little is known about Cd-S stretching frequencies. The assignments for the 94 cm^{-1} i.r. band and the 104 cm^{-1} Raman band to the Cd-N bending frequencies and those of the 78 cm⁻¹ i.r. band and 80 cm⁻¹ Raman band to the Cd-S bending frequencies follow from the assignments for the stretching modes. The assignment of the 65 cm⁻¹ Raman band is uncertain.

The significant feature of the i.r. and Raman spectra of cadmium(II) thiocyanate is the lack of coincidence in the skeletal vibrational modes. The spectral features, thus, clearly indicate a centrosymmetric octahedral coordination polyhedron around cadmium. This study demonstrates that the

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Table 1. Observed i.r. and Raman frequencies for solid Cd(SCN)₂ in the 4000-50 cm⁻¹ region

Infrared	Raman	Assignment
2148 s 2141 s 2096 sh 900 w,b	$ \begin{array}{c} 2148 \text{ sh} \\ 2142 \text{ s} \\ - \end{array} \right\} $	ν _{CN}
760 mw	760 m	$\nu_{\rm CS}$
460 mw	458 w	
448 ms	450 w	δ_{SCN}
444 ms		
204 vs	_	VacaN(A,)
	198 s	V _{SCdN(A,)}
	158 m,b	$\nu_{scds(R_{-})}$
140 vs,b	_	$\nu_{acas(F)}$
	131 s	V _{SCdS(A)}
94 vs,b	104 w	$\delta_{CdN(E_a)}$
78 vs,b	80 w	$\rho_{r(E_{-})}$
	65 w	lattice mode

Descriptions of abbreviations: b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak; ν_a , antisymmetric stretch; ν_s , symmetric stretch; δ , bend; ρ_r , rock.

combined infrared and Raman spectral data in the region of the thiocyanate vibrations as well as the skeletal vibrations are required for arriving at reliable conclusions on the mode of bonding of the thiocyanate in metal thiocyanates and their complexes.

EXPERIMENTAL

Preparation of Cadmium(II) thiocyanate. It was prepared from the metathetical reaction of cadmium sulphate with barium(II) thiocyanate which was prepared from the reaction of barium(II) hydroxide and ammonium thiocyanate. Ba(OH)₂ · 8H₂O (31.56 g) was added to 11 distilled water. To this mixture was added a solution of NH₄SCN(15.24 g) in 200 ml distilled water and the reaction mixture was refluxed to remove all the dissolved ammonia. The water was evaporated and the resulting Ba(SCN)₂ was recrystallized from ethanol. A solution of CdSO₄ · 8/3 H₂O (6.41 g) in boiling distilled water (50 ml) was added dropwise, with stirring, to a solution of Ba(SCN)₂ (6.34 g) in 200 ml boiling distilled water. After stirring for several hours, the precipitated BaSO₄ was filtered off and the filtrate was evaporated. The resulting Cd(SCN)₂ was recrystallized from ethanol. Anal. calcd. for Cd(SCN)₂: C, 10.50; N, 12.25; S, 28.05. Found: C, 10.40; N, 12.00; S, 28.00.

Spectral Measurements. Infrared spectra were obtained with a Perkin-Elmer 180 double beam spectrophotometer on samples prepared as mulls in Nujol and halo-carbon oil. The samples were placed between KRS-5 and polyethylene discs. The Raman spectra were obtained with a Jarell-Ash Raman spectrometer using the 5145Å excitation line of a Spectra-Physics argon ion laser (400 mW). The sample was packed in a glass capillary tube. The observed infrared and Raman frequencies are accurate within $\pm 2 \text{ cm}^{-1}$.

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REFERENCES

- R. A. BAILEY, S. L. KOZAK, T. W. MICHELSEN and W. N. MILLS, *Coord. Chem. Rev.* 6, 407 (1971) and references therein.
- [2] A. H. NORBURY, Adv. Inorg. Chem. Radiochem. 17, 231 (1975) and references therein.
- [3] R. G. GOEL and W. O. OGINI, Inorg. Chem. 16, 1968 (1977).
- [4] M. CANNAS, G. CARTA, A. CRISTINI and G. MARON-GIU, J. Chem. Soc. Dalton Trans. 300 (1976).
- [5] R. J. H. CLARK and C. S. WILLIAM, *Inorg. Chem.* 4, 350 (1965).
- [6] J. REEDUK and W. L. GROENWALD, Rec. Trav. Chim 87, 1079 (1968).