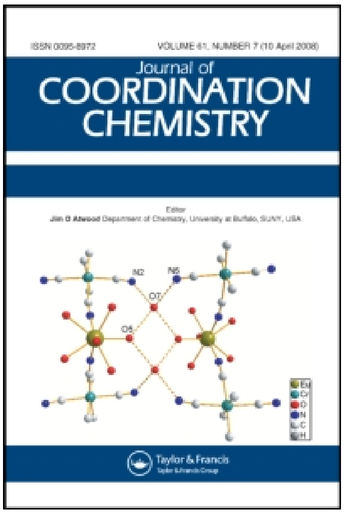
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE PREPARATION AND CHARACTERIZATION OF Cd(XCN)$_4$M TYPE COMPOUNDS

M. Nagao[a]; H. Inoue[a]; S. Yanagisawa[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Keio University, Yokohama, Japan

To cite this Article Nagao, M. , Inoue, H. and Yanagisawa, S.(1980) 'THE PREPARATION AND CHARACTERIZATION OF Cd(XCN)$_4$M TYPE COMPOUNDS', Journal of Coordination Chemistry, 10: 1, 29 — 34
To link to this Article: DOI: 10.1080/00958978008079847
URL: http://dx.doi.org/10.1080/00958978008079847

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1980, Vol. 10, pp. 29–34
0095-8972/80/1001-0029 $04.50/0

© 1980 Gordon and Breach Science Publishers, Inc.
Printed in Great Britain

THE PREPARATION AND CHARACTERIZATION OF $Cd(XCN)_4M$ TYPE COMPOUNDS

M. NAGAO, H. INOUE and S. YANAGISAWA

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan

(*Received January 5, 1979; in final form April 23, 1979*)

A series of compounds of the type $Cd(XCN)_4M$ (X=S and Se; M=Mn, Fe, Co and Zn) have been prepared and characterized. These compounds crystallize in the tetragonal system: space group $I\bar{4}-S_4^2$. The bidentate thiocynate and selenocyanate ligands coordinate to the "hard" M(II) ions through the nitrogen atom and the "soft" Cd(II) ion through the sulfur or selenium atom. The Cd–Se bond in $Cd(XCN)_4M$ is slightly stronger than the Cd–S bond while the M–NCSe bond is slightly weaker than the M–NCS bond. The M(II) ions tetrahedrally coordinated by the nitrogen end of XCN^- are in the high spin state. The –NCS and –NCSe ligands are located at about the same place in the spectrochemical series.

Downloaded At: 20:29 23 January 2011

INTRODUCTION

In recent years a large number of coordination compounds containing the thiocyanate and selenocyanate ions as ligands have been synthesized and characterized. Both of these ligands are well known to function as a bridging ligand because they coordinate to the metal ion "a" through the nitrogen atom and "b" through the sulfur or selenium atom[1]. The investigations on coordination compounds containing bridging ligands have begun with the preparation of $Hg(SCN)_4M$ (M = Co and Cu) and $Ag_2(SCN)_4Co$ by Rosenheim and Cohn[2]. More recently a series of compounds of the type $Hg(XCN)_4M$ (X = S and Se; M = Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd) have been characterized by means of magnetic moment, X-ray powder diffraction, infrared and electronic spectra[3–13]. In particular, the crystal structure of $Hg(SCN)_4Co$[14] and $Hg(SCN)_4Cu$[15] has received relatively much attention. However, there have been few studies concerning cadmium compounds of the type $Cd(XCN)_4M$ except that the preparative methods and infrared spectral data of $Cd(SCN)_4Co$ and $Cd(SCN)_4Ni$ have been reported[10,16]. This type of compounds seem to be very interesting because they are expected to possess the same structure as mercury compounds of the type $Hg(XCN)_4M$. The purpose of the present paper is to describe the preparation of $Cd(XCN)_4M$ (X = S and Se; M = Mn, Fe, Co and Zn) and to discuss their structure and chemical bonding in comparison with mercury compounds of the type $Hg(XCN)_4M$.

EXPERIMENTAL

Preparation of Compounds

All metal salts used here were of reagent grade and used without further purification. Potassium selenocyanate was purified prior to use according to the conventional method.

$K_2Cd(XCN)_4$ (X = S and Se). An aqueous solution of a stoichiometric amount of KXCN (0.02 mol in 10 ml) was added to a solution of $CdCl_2 \cdot 2.5H_2O$ in water (0.005 mol in 15 ml). The solution obtained was evaporated to dryness, followed by extraction with ethanol (50 ml) and the extractant was again brought to dryness. This procedure was repeated several times in order to separate KCl from $K_2Cd(XCN)_4$. Anal. Calcd. for $K_2Cd(SCN)_4$: Cd, 26.6. Found: Cd, 26.3. Calcd. for $K_2Cd(SeCN)_4$: Cd, 18.4; Se, 51.7. Found: Cd, 18.3; Se, 51.7.

$Cd(SCN)_4M$ (M = Co and Zn). A solution of hydrated metal chloride in ethanol (0.005 mol in 20 ml) was mixed with that of a stoichiometric amount of $K_2Cd(SCN)_4$ in ethanol (0.005 mol in 50 ml). After the precipitate of potassium chloride was separated by filtration, the resulting filtrate was evaporated

Downloaded At: 20:29 23 January 2011

slowly to precipitate the desired compound. The precipitate obtained was filtered off and washed with ethanol and ether successively. Anal. Calcd. for $Cd(SCN)_4Co{\cdot}6.7H_2O$:Cd, 21.4; Co, 11.2. Found:Cd, 21.5; Co, 11.2. Calcd. for $Cd(SCN)_4Zn{\cdot}3.6H_2O$: Cd, 23.6; Zn, 13.8. Found:Cd, 24.1; Zn, 13.5.

$Cd(SCN)_4M$ (M = Mn and Fe). The ethanol solution of $Cd(SCN)_4M$ (M = Mn and Fe) prepared by the same method as described for $Cd(SCN)_4M$(M = Co and Zn) was evaporated to dryness. The residue obtained was suspended in nitromethane (30 ml), refluxed for about one hr. at 120 °C, filtered off and then washed successively with nitromethane, ethanol and ether. Anal. Calcd. for $Cd(SCN)_4Mn$: Cd, 28.1; Mn, 13.7. Found:Cd, 27.8; Mn, 13.4. Calcd. for $Cd(SCN)_4Fe{\cdot}1.1H_2O$:Cd, 26.6; Fe, 13.3. Found:Cd, 26.7; Fe, 13.1.

$Cd(SeCN)_4M$ (M = Mn, Fe and Zn). The ethanol solution of $Cd(SeCN)_4M$ (M = Mn, Fe and Zn) was prepared by the method similar to that in $Cd(SCN)_4M$ (M = Co and Zn). After evaporation of the solution to an oily product, the desired compound was precipitated by addition of ether to the oil, filtered off and washed with ether. Anal. Calcd. for $Cd(SeCN)_4Mn{\cdot}1.6H_2O$:Cd, 18.2; Mn, 8.9; Se, 51.3. Found:Cd, 18.1; Mn, 9.0; Se, 51.2. Calcd. for $Cd(SeCN)_4Fe{\cdot}0.2H_2O$:Cd, 19.0; Fe, 9.4; Se, 53.4. Found:Cd, 19.2; Fe, 9.4; Se, 53.1. Calcd. for $Cd(SeCN)_4Zn$:Cd, 18.8; Zn, 10.9; Se. 52.8. Found:Cd, 18.7; Zn, 10.7; Se, 53.3.

$Cd(SeCN)_4Co$. A solution of $K_2Cd(SeCN)_4$ in ethanol (0.005 mol in 10 ml) was added to a solution of $CoCl_2{\cdot}6H_2O$ in ethanol (0.005 mol in 10 ml) on heating. The desired compound precipitated immediately was filtered off and washed successively with ethanol and ether. Anal. Calcd. for $Cd(SeCN)_4Co$:Cd, 19.0; Co, 10.0; Se, 53.4. Found:Cd, 19.1; Co, 9.8; Se, 53.4.

It was necessary to handle two iron containing compounds in a dry nitrogen atmosphere because both of them tend to be easily oxidized. All prepared compounds were dried over $CaCl_2$ in a desiccator.

Physical Measurements

The X-ray powder diffraction patterns were measured with a Rigaku–Denki X-ray diffractometer. The lattice constants were determined using Cu-Kα radiation (λ = 1.5418 Å) and Si as a standard. Because both $Cd(SeCN)_4Mn$ and $Cd(SeCN)_4Fe$ were very unstable in the atmosphere, the measurements of these compounds were carried out with a cover of parafilm. The infrared spectra were recorded with a Hitachi–Perkin Elmer 225 ir spectrophotometer in the range 4000–400 cm^{-1} by the KBr disk method and in the range 400–200 cm^{-1} by the CsI disk method. The wavenumbers recorded here were calibrated using polystyren film. The magnetic susceptibilities were measured by the Gouy method. The Gouy tubes were calibrated with $Hg(SCN)_4Co$ ($\chi = 16.44 \times 10^{-6}$ cgs unit at 20 °C[17]) and diamagnetic corrections were calculated with the Pascal constants[18]. The diffuse reflection spectra for the powdered samples were measured in the range 13000–33000 cm^{-1} using the Hitachi–Perkin Elmer 139 UV-VIS spectrophotometer with the standard integrating sphere attachment and alumina as a reference.

RESULTS AND DISCUSSION

The X-ray powder diffraction patterns of $Cd(XCN)_4M$ (X = S and Se; M = Mn, Fe, Co and Zn) are very similar to that of $Hg(SCN)_4Co$ reported by Jeffery[14], although some diffraction peaks were weak or missing in $Cd(SeCN)_4M$ (M = Mn and Fe) probably due to the influence of parafilm used for measurements. This indicates that $Cd(XCN)_4M$ type compounds are isomorphous with $Hg(SCN)_4Co$; the $Cd(XCN)_4M$ type compounds belong to space group $I\bar{4}$–S_4^2 and contains two formula units per unit cell. As shown in Fig. 1, the thiocyanate or selenocyanate

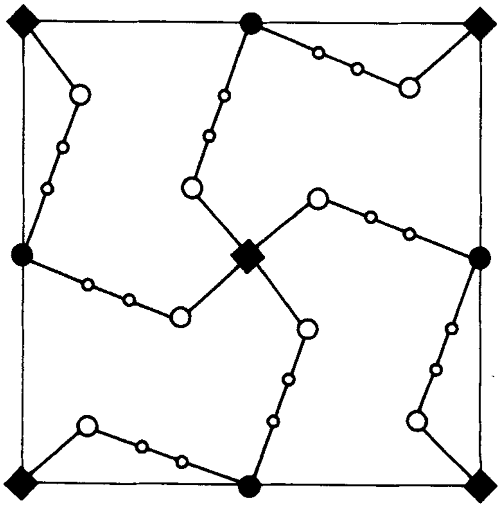


FIGURE 1 The unit cell of Cd $(XCN)_4M$, projected on the c-face.
▪ Cd: 0, 0, 0 ○ X: 0.15, 0.13, 0.28
• M: 1/2, 0, 1/4 or 1/2, 0, 3/4 ○ C or N.

Downloaded At: 20:29 23 January 2011

TABLE I
Lattice constants, atomic distances and magnetic moments

Compound	Lattice constant (Å) a	 c	Atomic distance of the M-X (Å)	Magnetic moment (B.M.)
Cd(SCN)$_4$Mn	11.36	4.20	2.54	5.97
Cd(SCN)$_4$Fe	11.26	4.25	2.53	5.23
Cd(SCN)$_4$Co	11.17	4.33	2.53	4.62
Cd(SCN)$_4$Zn	11.15	4.37	2.53	diamagnetic
Cd(SeCN)$_4$Mn	11.56	4.48	2.62	–
Cd(SeCN)$_4$Fe	11.46	4.50	2.60	–
Cd(SeCN)$_4$Co	11.33	4.64	2.60	4.44
Cd(SeCN)$_4$Zn	11.32	4.68	2.60	diamagnetic

ion plays a role of bidentate ligands in the unit cell, i.e. sulfur or selenium and nitrogen ends coordinate to Cd and M, respectively.

The lattice constants of our compounds are summarized in Table I. It is worth noting that the lattice constant a decreases with the increase in the atomic number of M whereas the lattice constant c is quite in the reverse. The same tendency was found for the lattice constants of Hg(XCN)$_4$M (X = S and Se; M = Mn, Fe, Co and Zn)[7,8,9,11,12,13].

The atomic distance between Cd and X (X = S and Se) is calculated from the lattice constant on the assumption that the coordinates Cd(0, 0, 0), X(0.15, 0.13, 0.28) and M(1/2, 0, 1/4) or (1/2, 0, 3/4) in Cd(XCN)$_4$M are the same as those of Hg, S and Co in Hg(SCN)$_4$Co reported by Jeffrey[14]. The atomic distances Cd–S and Cd–Se calculated are listed in Table I. Both types of atomic distances are hardly affected by M and in good agreement with the Cd–S distance (2.52 Å) and the Cd–Se distance (2.62 Å) estimated from the tetrahedral covalent radii by Pauling[19], indicating that the bonding between Cd–X is covalent.

The infrared absorption bands of compounds containing XCN$^-$ as ligand were observed in the range 4000 to 400 cm^{-1}. These bands are mainly due to the fundamental vibrations such as the C–N and C–X stretching and N–C–X deformation modes. The absorption bands assignable to the M–N and Cd–X stretching modes were observed in the range 400 to 200 cm^{-1}. On the other hand, the M–N–C, Cd–X–C, N–M–N and X–Cd–X deformation modes must be located out of our experimental region. The absorption frequencies of Cd(XCN)$_4$M

TABLE II
Infrared spectra of the compounds

Compound	ν(CN)	ν(CX)	δ(NCX)	ν(MN)	ν(CdX)
Cd(SCN)$_4$Mn	2,122 (VS)	782 (W)	474 (S) 451 (S)	280 (S)	224 (S)
Cd(SCN)$_4$Fe	2,140 (VS) 2,121 (S) 2,090 (sh)	788 (W)	473 (S) 452 (S)	291 (S) 280 (S)	
Cd(SCN)$_4$Co	2,147 (VS) 2,136 (S)	790 (W)	470 (S) 450 (S)	300 (S)	225 (S)
Cd(SCN)$_4$Zn	2,160 (VS)	790 (W)	476 (S) 452 (S)		224 (M)
Cd(SeCN)$_4$Mn	2,129 (VS) 2,117 (S) 2,074 (S)	620 (S)	420 (M) 406 (M)	235 (M)	220 –207 (mult, M)
Cd(SeCN)$_4$Fe	2,130 (VS) 2,071 (S)	631 (S)	420 (M) 407 (M)	233 (M)	218 (S)
Cd(SeCN)$_4$Co	2,140 (VS)	634 (S)	420 (M) 407 (M)	249 (M)	224 (M)
Cd(SeCN)$_4$Zn	2,154 (VS)	628 (S)	420 (M) 406 (M)		

(unit: cm^{-1})
VS = very strong S = strong M = medium W = weak sh = shoulder mult = multiplet

Downloaded At: 20:29 23 January 2011

type compounds are presented in Table II. The absorption bands were assigned by comparing the spectra with those reported on $Hg(SCN)_4Co$ in the literature[10,20]. The overtone of δ_{NCX} was observed around 900 cm^{-1} and 800 cm^{-1} in the compounds containing thiocyanate and selenocyanate ligands, respectively. However, these overtone bands were not presented in Table II for brevity's sake. The C–N stretching bands of $Cd(XCN)_4M$ type compounds were observed in the range 2070–2160 cm^{-1}. The C–N stretching bands of $Cd(SCN)_4M$ are shifted to higher frequencies by 70–110 cm^{-1} compared with that of KSCN, while the C–N stretching frequencies of $Cd(SeCN)_4M$ are higher by 50–85 cm^{-1} than those of k_{SeCN}. With regard to C–X stretching mode, the C–S and C–Se stretching bands were observed in the range 780–790 cm^{-1} and 620–635 cm^{-1}, respectively. These bands lie intermediate between KXCN and $M(NCX)_4^{2-}$. The characteristic shift of these fundamental frequencies upon formation of coordination bond of XCN was pointed out by Lewis et al.[21] They considered nine possible forms for XCN$^-$ ion and coordinated XCN (see Fig. 2), implying that form (g) is important for M–XCN bond, while for M–NCX bond form (f) and (d) are important. According to this interpretation the greater increase relative to free ion in ν_{CN} and the increase relative to the free ion but to the lesser amount than the N–bonded compounds in ν_{CX} should be observed for M_1–NCX–M_2 bridging ligands. Consequently, the shifts of ν_{CN} and ν_{CX} observed in the present case are evidence for the existence of the linkage structure Cd–XCN–M.

The ν_{CdS} bands of $Cd(SCN)_4M$ were observed at about 225 cm^{-1} while the ν_{CdSe} bands of $Cd(SeCN)_4M$ appeared at about 220 cm^{-1}. The force constant k_{CdX} can be calculated as a first approximation from the equation of $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ by using reduced mass μ and frequency ν_{CdX} (X = S and Se). The calculated values of force constants are presented in Table III, demonstrating that the Cd–Se bond is slightly stronger than the Cd–S bond. The same tendency was observed in $Hg(XCN)_4M$ type compounds and interpreted on the basis of hard and soft acids and bases theory in the previous paper[1,8]. The ν_{MN} bands of $Cd(SCN)_4M$ and $Cd(SeCN)_4M$ appeared in the range 280–300 cm^{-1} and 230–250 cm^{-1}, respectively. The force constant k_{MN} calculated by the same method as used for k_{CdX} has exhibited that the M–NCS bond is slightly stronger than the M–NCSe bond.

The effective Bohr magneton per M(II) of $Cd(SCN)_4M$ (M = Mn, Fe and Co) and $Cd(SeCN)_4Co$ was calculated from the magnetic susceptibilities at room temperature and presented in Table I. Although the calculated values are higher than corresponding spin-only values because of the spin-orbit coupling effect, they fall into the region characteristic of tetrahedral high-spin complexes of M(II)[22]. It appears that the M(II) ion tetrahedrally coordinated through the nitrogen ends of SCN and SeCN appears to be in the high-spin state. An attempt to obtain magnetic susceptibilities of $Cd(SeCN)_4Mn$ and $Cd(SeCN)_4Fe$ failed to give a reasonable magnetic moment because both compounds undergo rapid decomposition even in a nitrogen atmosphere.

The diffuse reflectance spectra of compounds of the type $Cd(XCN)_4M$ are presented in Fig. 3. The absorption bands observed in $Cd(SCN)_4Mn$ resemble closely those of the corresponding tetraisothiocyanatomanganate(II) ion reported in the literatures[23], although each absorption band is slightly shifted to higher frequencies upon formation of $Cd(SCN)_4Mn$ from $K_2[Mn(NCS)_4]$. Therefore, the spin-forbidden bands may be assigned on the basis of

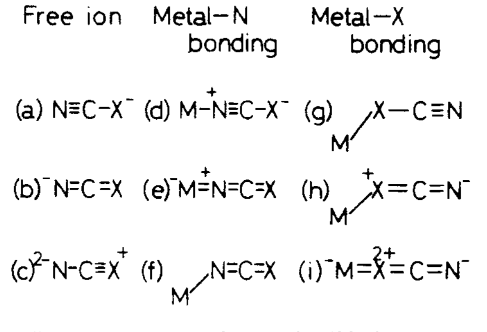


FIGURE 2 The possible forms of XCN$^-$ ion and coordinated XCN.

TABLE III
Comparison of estimated force constants

Compound	k_{MN}	k_{CdX}
$Cd(SCN)_4Mn$	0.52	0.74
$Cd(SCN)_4Fe$	0.56–0.52	–
$Cd(SCN)_4Co$	0.60	0.74
$Cd(SCN)_4Zn$	–	0.74
$Cd(SeCN)_4Mn$	0.36	1.29–1.14
$Cd(SeCN)_4Fe$	0.36	1.27
$Cd(SeCN)_4Co$	0.41	1.34
$Cd(SeCN)_4Zn$	–	–

(unit: mdyn/Å)

Downloaded At: 20:29 23 January 2011

the term diagram in T_d symmetry as follows: $^6A_1 \rightarrow {}^4T_1(G)$ at 20,400 cm^{-1}; $^6A_1 \rightarrow {}^4T_2(G)$ at 22,200 cm^{-1}; $^6A_1 \rightarrow {}^4E, {}^4A_1(G)$ at 23,200 cm^{-1}; $^6A_1 \rightarrow {}^4T_2(D)$ at 25,600 cm^{-1}; $^6A_1 \rightarrow {}^4E(D)$ at 27,400 cm^{-1}. Unfortunately, the corresponding selenocyanate compound Cd(SeCN)$_4$Mn fails to give a reliable spectrum due to its high sensitivity to air exposure. An intense charge-transfer band was observed for Cd(SCN)$_4$Fe at 28,600 cm^{-1}. However, the absorption band of the transition $^5E \rightarrow {}^5T_2$ characteristic of the tetrahedral iron(II) complexes was not found within the present experimental region (13,000–33,000 cm^{-1}). It is probable that this type of d–d transition is located around 5,000 cm^{-1} for Cd(SCN)$_4$Fe in view of the observation for Hg(SCN)$_4$Fe by Scaife[7]. Another iron compound Cd(SeCN)$_4$Fe was too susceptible to air oxidation to measure its diffuse reflectance spectrum. An intense absorption band, which is observed in Cd(SCN)$_4$Co and Cd(SeCN)$_4$Co at 16,900 and 17,000 cm^{-1} respectively, is assigned to the d–d transition $^4A_2 \rightarrow {}^4T_1(P)$ in the tetrahedral weak field. As expected from the cases of Hg(SCN)$_4$Co and Hg(SeCN)$_4$Co[5], the energies of the transition $^4A_2 \rightarrow {}^4T_1(P)$ appear to be essentially the same in both Cd(SCN)$_4$Co and Cd(SeCN)$_4$Co, indicating that the thiocyanate and selenocyanate ligands are at about the same place in the spectrochemical series if their nitrogen end takes part in coordination. The spin-allowed transition $^4A_2 \rightarrow {}^4T_1(P)$ is shifted to higher frequencies on going from $K_2[Co(NCX)_4]$ to Cd(XCN)$_4$Co. This is consistent with the fact that the bridge-formation of thiocyanate and selenocyanate ligands is accompanied by an increase in the Δ value of the $Co(NCS)_4^{2-}$ and $Co(NCSe)_4^{2-}$ moieties[13].

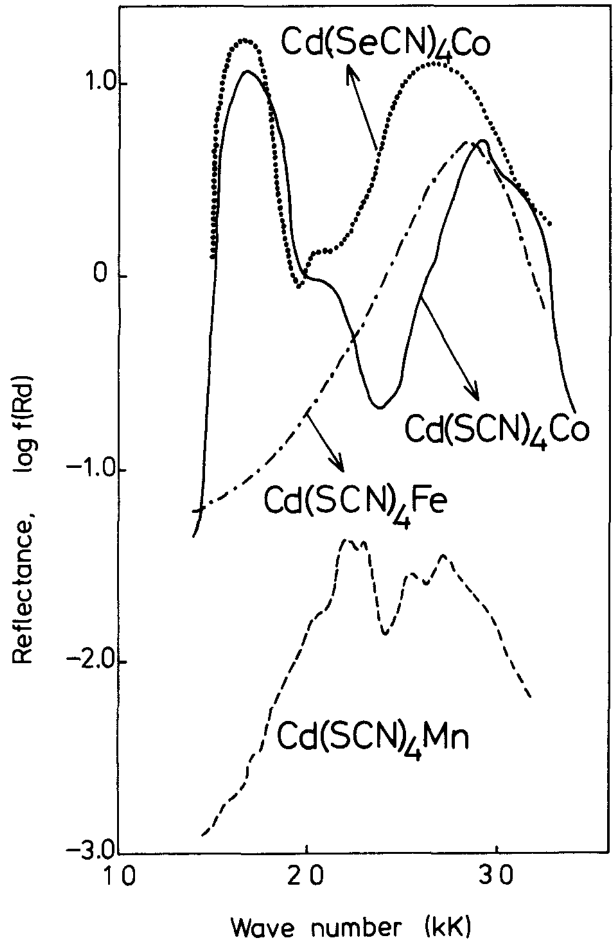


FIGURE 3 Reflectance spectra of Cd(XCN)$_4$M.

The first charge-transfer band in the near-ultraviolet region was observed at higher frequencies in Cd(SCN)$_4$M than in Cd(SeCN)$_4$M. This observation is in good agreement with the tendency expected from the terminal tetraisothiocyanato- and tetraisoselenocyanatometalate(II) ions[24]. This type of charge-transfer band was shifted in iron and cobalt compounds to lower energies with respect to the corresponding terminal tetraisothiocyanato- and tetraisoselenocyanatometalate(II) ions upon the bridge-formation through the XCN$^-$ ligand. However, such charge-transfer bands could not be observed in manganese or zinc compounds because the difference between the electro-negativity of the central metal ions and the optical electronegativity of ligands[24] is too large. The charge-transfer band from the S- or Se-coordinated ligand to the cadmium ion should be located at much higher frequencies since the difference between the electronegativity of the cadmium ion and the opticalelectronegativity of –SCN and –SeCN is larger than that between the electronegativity of the M(II) ions and the opticalelectronegativity of –NCS and –NCSe. In fact, this type of charge-transfer bands were absent in the present experimental region. Accordingly, the charge-transfer bands observed in the iron and cobalt compounds are ascribed to the charge-transfer from the –NCX ligands to the M(II) ion.

REFERENCES

1. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
2. A. Rosenheim and R. Cohn, *Z. Anorg. Allg. Chem.*, **27**, 285 (1901).
3. A. Tramer, *J. Chim. Phys.*, **59**, 232 (1962).

4. Yu. Ya. Kharitonov and V. V. Skopenko, *Zh. Neorg. Khim.*, **10**, 1191 (1965); Russ. *J. Inorg. Chem.*, **10**, 645 (1965).
5. A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).
6. R. M. Alasaniya, V. V. Skopenko and G. V. Tsintsadge, *Tr. Gruz. Politekh. Inst.*, 21 (1967).
7. D. E. Scaife, *Inorg. Chem.*, 6, 625 (1967).
8. M. Nagao, H. Inoue and S. Yanagisawa, *J. Inorg. Nucl. Chem.*, **40**, 1686 (1978).
9. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).
10. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).
11. E. Frasson, A. Turco and C. Panattoni, *Gazz. Chim. Ital.*, **91**, 750 (1961).
12. G. A. Tsintsadze, V. V. Skopenko and A. E. Shvelashvili, *Soobshch. Akad. Nauk. Gruz. SSR.*, **41**, 337 (1966).
13. F. A. Cotton, D. M. L. Goodgame, M. Goodgame and T. E. Hass, *Inorg. Chem.*, **1**, 565 (1962).
14. J. W. Jeffery, *Nature (London)*, 159, 610 (1947).
15. C. Friebel and M. J. G. Garmendia, *Z. Naturforsch. Tail B*: 883, 30 (1972).
16. R. A. Bailey and T. W. Michelsen, *J. Inorg. Nucl. Chem.*, **34**, 2671 (1972).
17. B. N. Figgis and R. S. Nyholm, *J. Chem Soc.*, 4190 (1958).
18. P. W. Selwood, *Magnetochemistry*, 2nd Ed (Interscience Publishing. Co., New York, 1956), p. 91.
19. L. Pauling, *The nature of the chemical bond*, 3rd Ed (Cornell University press, 1960), p. 224.
20. A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).
21. J. Lewis, R. S. Nyholm and P. W. Smith. *J. Chem. Soc.*, 4590 (1961).
22. J. Lewis and R. G. Wilkins, *Modern coordination chemistry* (Interscience Publishing. Co., New York, 1960), p. 406.
23. D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 268 (1965).
24. H. H. Schmidtke, *Ber. Bunsenger. Phys. Chem.*, 71, 1138 (1967).

Downloaded At: 20:29 23 January 2011