CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7, ENGLAND

Infrared Spectra (400–200 Cm.$^{-1}$) of Some Thiocyanate and Isothiocyanate Complexes

BY D. FORSTER AND D. M. L. GOODGAME

Received January 5, 1965

The infrared spectra of compounds containing the following anions: $M(NCS)_4{}^{2-}$ where M = Mn^{II} to Zn^{II}; $M(NCS)_6{}^{n-}$ where M = Mn^{II}, Ni^{II}, Cr^{III}, Fe^{III}, and Mo^{III}; $M(SCN)_4{}^{n-}$ where M = Pd^{II}, Pt^{II}, Hg^{II}, and Au^{III}; $Pt(SCN)_6{}^{2-}$; and of the compounds $M^{II}Hg(SCN)_4$, where M = Mn to Zn, and $CoCd(SCN)_4$, have been determined in the range 400–200 cm.$^{-1}$. Bands assignable as essentially metal–nitrogen stretching frequencies were observed for all the isothiocyanato complexes, and "metal–sulfur stretches" were found in this region for most of the thiocyanato complexes. The spectra are discussed on the basis of the known or presumed structures of the compounds.

Introduction

The infrared spectra of metal "thiocyanate" complexes have been studied in recent years by several groups of workers[1] in order to provide criteria for distinguishing between N- and S- coordination of the NCS group. Hitherto these studies have been restricted to the region >400 cm.$^{-1}$ and have concerned what are essentially the internal modes of the thiocyanate group. Recently we examined the infrared spectra of some isocyanato complexes[2] and observed strong bands in the region 450–200 cm.$^{-1}$ due to modes with predominantly metal–nitrogen stretching character. It appeared worthwhile to investigate the possibility of differentiating between thiocyanato and isothiocyanato complexes by means of their infrared spectra in this region, and we report here some results for compounds containing $M(NCS)_x{}^{n-}$ or $M(SCN)_x{}^{n-}$ anions, and also for complexes containing bridging thiocyanate groups.

Experimental

The infrared spectra were obtained with a Grubb-Parsons grating spectrometer, Type DM.2, using Nujol mulls on polythene plates. Bands due to the cations were identified from spectra of the cation halides.

Compounds.—Salts of large quaternary cations were used in nearly all cases to avoid the presence of water of solvation, which often occurs with the salts of alkali metal cations prepared from aqueous solution. Moreover, some of the complex anions studied can be formed only with these large, organic cations. The preparations of most of the compounds either have been described elsewhere[3–5] or were carried out according to methods reported in the literature.[6] The tetramethylammonium salts of the anions $Cr(NCS)_6{}^{3-}$, $Pd(SCN)_4{}^{2-}$, $Pt(SCN)_4{}^{2-}$, $Pt(SCN)_6{}^{2-}$, and $Au(SCN)_4{}^{-}$ were prepared by mixing aqueous solutions of the corresponding K^+ salts with $[(CH_3)_4N]NCS$. Analyses are given in Table I. A specimen of $[(CH_3)_4N]_3Mo(NCS)_6$ was kindly supplied by Mr. N. Payne.

TABLE I

ANALYTICAL DATA FOR SOME OF THE COMPLEXES

Formula	Calcd., %			Found, %		
	C	H	N	C	H	N
$[(CH_3)_4N]_3Cr(NCS)_6$	34.73	5.79	20.26	34.86	5.84	20.14
$[(CH_3)_4N]_2Pd(SCN)_4$	29.60	4.93	...	29.32	4.80	...
$[(CH_3)_4N]_2Pt(SCN)_4$	25.04	4.17	...	24.62	3.83	...
$[(CH_3)_4N]_2Pt(SCN)_6$	24.31	3.47	16:20	23.98	3.76	16.36
$[(CH_3)_4N]Au(SCN)_4$	19.09	2.39	13.91	18.46	2.38	13.75

Results and Discussion

Complexes of the Type $(cation)_2M(NCS)_4$.—The infrared data (200–400 cm.$^{-1}$) for some complexes of stoichiometry $(cation)_2M(NCS)_4$, where M = Mn^{II} to Zn^{II}, are listed in Table II. X-Ray structural studies have shown[7] that in the potassium salts of $Co(NCS)_4{}^{2-}$ and $Zn(NCS)_4{}^{2-}$ the nitrogen atoms are arranged tetrahedrally around the divalent metal ions. Similar structures have been suggested, on the basis of electronic spectra, for the compounds of $Co(NCS)_4{}^{2-}$ with large organic cations[5] and for the related complexes of Mn^{II} and Fe^{II}.[3] Thus the strong band observed in the region 280–310 cm.$^{-1}$ for the ions $M(NCS)_4{}^{2-}$, where M = Mn^{II}, Fe^{II}, Co^{II}, and Zn^{II}, may be assigned as ν_{11}, the MN_4 degenerate stretch

TABLE II

INFRARED DATA (CM.$^{-1}$)[a] FOR SOME COMPOUNDS $(cation)_2M(NCS)_4$

$[n\text{-}C_4H_9(C_6H_5)_3P]_2Mn(NCS)_4$	287 br
$[(C_2H_5)_4N]_2Fe(NCS)_4$	293
$[(CH_3)_4N]_2Co(NCS)_4$	304
$[(C_2H_5)_4N]_2Co(NCS)_4$	307
$[n\text{-}C_4H_9(C_6H_5)_3P]_2Co(NCS)_4$	303
$(cat^{2+})Co(NCS)_4$[b]	303
$(cat^{2+})Ni(NCS)_4$ blue form	309, 281 sh
$[(C_6H_5)_4As]_2Ni(NCS)_4$ blue-green form	309[c]
$[(C_6H_5)_4As]_2Ni(NCS)_4$ olive-yellow form	294, 266 m; ~230 ms, br
$[(CH_3)_4N]_2Ni(NCS)_4$	269, ~235 br
$[(C_2H_5)_4N]_2Cu(NCS)_4$	327, 249 w
$(cat^{2+})Cu(NCS)_4$	313, 294
$[(CH_3)_4N]_2Zn(NCS)_4$	280

[a] All bands are strong unless denoted otherwise. [b] cat^{2+} = $[p\text{-xylylenebis(triphenylphosphonium)}]^{2+}$. [c] Asymmetric to lower energy.

---

[1] M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959); P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960); J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961); A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[2] (a) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965); (b) *ibid.*, 1286 (1965).

[3] D. Forster and D. M. L. Goodgame, *ibid.*, 268 (1965).

[4] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, in press.

[5] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

[6] H. E. Williams, "Cyanogen Compounds," 2nd Ed., Edward Arnold, 1948; A. Rosenheim and R. Cohn, *Z. anorg. allgem. Chem.*, **27**, 280 (1901); H. Grossmann, *Ber.*, **35**, 2665 (1902).

[7] G. S. Zhdanov and Z. V. Zvonkova, *Zh. Fiz. Khim.*, **24**, 1339 (1950); Z. V. Zvonkova, *ibid.*, **26**, 1798 (1952).

of a system $M(NCX)_4$ with T_d symmetry.[2a,8] This description, and those used subsequently in this paper, solely in terms of metal–donor atom vibrations is used for convenience, since the actual modes responsible for these infrared bands probably will not have pure metal–donor atom character.

The observation of a single band for the Fe^{II}, Co^{II}, and Zn^{II} complexes suggests that any deviations from T_d symmetry in the anions are small. For the Mn^{II} complex the band is distinctly broader and is asymmetric to lower energy, which may indicate some departure from T_d symmetry. It may be noted that this complex is not isomorphous with its cobalt(II) analog.[3]

Four different $Co(NCS)_4{}^{2-}$ salts were examined, but alteration of the cation caused little change in the position of ν_{11}. The energies of the ν_{11} bands for the Mn^{II}, Fe^{II}, Co^{II}, and Zn^{II} complexes vary with the identity of the central metal ion in much the same way as those of ν_3 for the corresponding $MCl_4{}^{2-}$ ions.[9] The values of ν_{11} for the tetrahedral $M(NCS)_4{}^{2-}$ ions are 30–40 cm.$^{-1}$ lower than those of the analogous $M(NCO)_4{}^{2-}$ ions.[2a] This can be attributed mainly to the change in mass of the NCX group. A similar difference was observed for $Si(NCO)_4$ (727 cm.$^{-1}$)[8] and $Si(NCS)_4$ (598 cm.$^{-1}$).[10]

It has been suggested[4] from electronic spectral and magnetic studies that in the compounds $(cat^{2+})M(NCS)_4$,[11] where M = Ni (blue form) and Cu, and $[(C_6H_5)_4As]_2Ni(NCS)_4$ (blue-green form), the $M–N_4$ tetrahedra are distorted. Further support for this proposal is afforded by their infrared spectra. In the spectra of both $(cat^{2+})Ni(NCS)_4$ and $(cat^{2+})Cu(NCS)_4$ ν_{11} (triply degenerate in T_d) is split. This fact alone does not provide unambiguous confirmation that the $M–N_4$ tetrahedra are distorted, since nonlinear M–NCS groups could also give this result, but the combination of infrared and electronic spectral evidence suggests that the departure from T_d symmetry concerns the primary coordination sphere of the metal ion. In the case of the blue-green form of $[(C_6H_5)_4As]_2Ni(NCS)_4$ the ν_{11} band is not split but is broader to lower energy. Moreover the energy of the band maximum is higher than expected from consideration of the usual sequence of M–X stretching frequencies for tetrahedral complexes of Mn^{II} to Zn^{II}.[2a,9] This suggests that here too the $Ni(NCS)_4{}^{2-}$ ion is somewhat distorted from regularly tetrahedral geometry.

The compounds $[(C_6H_5)_4As]_2Ni(NCS)_4$ (olive-yellow form), $[(CH_3)_4N]_2Ni(NCS)_4$, and $[(C_2H_5)_4N]_2Cu(NCS)_4$ are thought[4] to have structures quite different from those of the other complexes listed in Table II and discussed above. It was suggested that in these compounds in the solid state there is anion association leading to a six-coordinate, tetragonal environment for the metal ion, probably composed of four nitrogen and two sulfur atoms, as in $HgCu(NCS)_4$.[12] However, the spectrum of the copper compound in this region is still relatively simple, consisting of one strong band at 327 cm.$^{-1}$ and a much weaker one at 249 cm.$^{-1}$. The frequency of the C–N stretch (2062 cm.$^{-1}$) for this complex suggests that if there is NCS bridging the Cu–S bonds are much weaker than are the Ni–S bonds in the tetragonal nickel complexes, where the C–N frequencies suggest strong NCS bridging (*e.g.*, 2123 (sh), 2114 cm.$^{-1}$ for $[(CH_3)_4N]_2Ni(NCS)_4$). It is possible therefore that the band at 327 cm.$^{-1}$ arises from a mode closely related to the M–N stretch, ν_{22}, for a planar (D_{4h}) $M(NCX)_4$ system,[8] due to four strong in-plane Cu–N bonds. From the results of our studies on S-bonded thiocyanate complexes (*vide infra*) we think it unlikely that the band at 249 cm.$^{-1}$ arises from a copper–sulfur stretching mode; in fact its weakness suggests that it may not be due to a fundamental.

The spectrum of $[(CH_3)_4N]_2Ni(NCS)_4$ consists of two bands at 269 and ~235 cm.$^{-1}$, the latter of which is rather broad, while that of the related tetraphenylarsonium salt is rather more complicated (Table II). In view of the uncertainty concerning the precise structures of these compounds, assignment of these low-energy bands will not be attempted. However, the very complexity of these spectra is in agreement with the idea of association of the $Ni(NCS)_4{}^{2-}$ anions, to provide a distorted octahedral ligand field.

$M(NCS)_6{}^{n-}$ Anions.—Nearly all the ions $M(NCS)_6{}^{n-}$ which have been studied show one strong band in the region 400–200 cm.$^{-1}$ (see Table III). In the case of the quinolinium salts the bands are rather broad and since they lie near the limit of the range of the spectrometer, their energies cannot be stated precisely.

TABLE III

INFRARED DATA (CM.$^{-1}$)[a] FOR SOME $M(NCS)_6{}^{n-}$ IONS

$(C_9H_8N)_4Mn(NCS)_6$	~222 br
$(C_9H_8N)_4Ni(NCS)_6$	~237 br
$[(CH_3)_4N]_4Ni(NCS)_6$	245
$[(C_2H_5)_4N]_4Ni(NCS)_6$	239
$[(CH_3)_4N]_3Fe(NCS)_6$	~298 sh, 272, ~233 sh
$[(CH_3)_4N]_3Cr(NCS)_6$	364
$[(CH_3)_4N]_3Mo(NCS)_6$	303

[a] All bands are strong.

The bands may be assigned as ν_{14}, the triply degenerate (T_{1u}) M–N stretch of a group $M(NCX)_6$ with O_h symmetry.[2b] As expected, the values of ν_{14} are higher for the trivalent than for the divalent metal ions. The spectrum of $[(CH_3)_4N]_3Fe(NCS)_6$ is rather more complicated than those of the other anions listed in Table III. As well as a strong band at 272 cm.$^{-1}$ there are two bands of medium intensity which appear as pronounced shoulders on either side of the main absorption. Since the ν_{14} mode is triply degenerate a molecular- or site-symmetry lower than O_h for $Fe(NCS)_6{}^{3-}$ could cause a splitting of this band. However the X-ray powder pattern of this compound is

---

[8] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

[9] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

[10] G. L. Carlson, *Spectrochim. Acta*, **18**, 1529 (1962).

[11] See note *b*, Table II.

[12] A. Korczynski, *Roczniki Chem.*, **36**, 1539 (1962).

virtually identical with that of its Cr^{III} analog, for which ν_{14} appears as a single, relatively sharp band, with no other detectable absorption down to 200 cm.$^{-1}$. In the absence of further data we cannot provide an unambiguous explanation for the spectrum observed for the Fe^{III} complex.

Thiocyanate Complexes.—The frequencies of the bands observed for the $M(SCN)_n^{x-}$ anions are listed in Table IV. They were found to be weaker than those of the isothiocyanate complexes. All the complexes except $K_2Hg(SCN)_4$ have a band of medium intensity in the range 280–305 cm.$^{-1}$; in the case of the Pd^{II} salt the band is split. We assign these bands to "metal–sulfur stretching" modes. Their formal designations will not be given, since, although the symmetries of the $M-S_x$ groupings probably approximate to D_{4h} (Pd^{II}, Pt^{II}, and Au^{III}) or O_h (Pt^{IV}), the nonlinearity expected for M–SCN will almost certainly result in over-all molecular symmetries lower than these. The frequencies of these bands for the Pd^{II}, Pt^{II}, Au^{III}, and Pt^{IV} thiocyanato anions fall very approximately half-way between the M–Cl and M–Br stretches of the analogous halo complexes[13–16] (*cf.*, for example, $PtCl_4^{2-}$ 320 cm.$^{-1}$, and $PtBr_4^{2-}$ 233 cm.$^{-1}$).[13]

TABLE IV

INFRARED DATA (CM.$^{-1}$) FOR SOME $M(SCN)_n^{x-}$ ANIONS

$[(CH_3)_4N]_2Pd(SCN)_4$	298 sh, 289 m, ~207 w, br
$[(CH_3)_4N]_2Pt(SCN)_4$	280 m, ~226 mw
$[(CH_3)_4N]Au(SCN)_4$	301 m, 277 vw, ~224 mw
$[(CH_3)_4N]_2Pt(SCN)_6$	282 m, 226 mw
$K_2Hg(SCN)_4$	~210 w, br

Since ν_3 (M–Cl) for $HgCl_4^{2-}$ is at 228 cm.$^{-1}$,[15] the metal–sulfur stretch for $K_2Hg(SCN)_4$ would be expected to lie below the limit of our range of study (200 cm.$^{-1}$). In agreement with this, we observed only one very weak band (at ~210 cm.$^{-1}$), which from its very low intensity is probably not a metal–sulfur absorption.

Several low-energy deformation modes are expected for these $M(SCN)_x^{n-}$ anions, because of the nonlinearity of the M–SCN grouping mentioned above. From our present data we cannot say, however, which of these may be responsible for the weak or medium-weak bands observed for the Pd^{II}, Pt^{II}, Au^{III}, and Pt^{IV} salts in the range 200–230 cm.$^{-1}$.

Complexes Containing Bridging NCS Groups.—One of the simplest types of compound containing bridging NCS groups is the series M^{II}Hg(SCN)$_4$ where M^{II} = Mn^{II} through Zn^{II}. We have examined the infrared spectra of these complexes and also of the related compound $CoCd(SCN)_4$, and the results are given in Table V.

It is known[17] that in $CoHg(SCN)_4$ the Co and Hg atoms are surrounded by four nitrogen and four sulfur atoms, respectively, in approximately tetrahedral arrangements. Thus the strong band at 303 cm.$^{-1}$ may be assigned to Co–N stretching analogous to the band observed for the $Co(NCS)_4^{2-}$ ion. The shoulder at 276 cm.$^{-1}$ may be ascribed to the removal of the degeneracy of this T_2 mode by the distortion of the $Co-N_4$ tetrahedron ($\angle NCoN = 117.6°$ and $105.6°$[17]). The compound $ZnHg(SCN)_4$ is isomorphous with the cobalt(II) analog,[18] and essentially similar structures have been suggested,[3] on the basis of electronic spectra, for the Mn^{II} and Fe^{II} compounds. Thus similar assignments may be made for the spectra of these complexes above 240 cm.$^{-1}$. Although there is no definite information available concerning the structure of $CoCd(SCN)_4$, the similarity of its infrared spectrum to that of $CoHg(SCN)_4$ and its blue color suggest that, here too, the cobalt ion is surrounded by four nitrogen atoms in an approximately tetrahedral array.

TABLE V

INFRARED DATA (CM.$^{-1}$) FOR SOME COMPOUNDS CONTAINING BRIDGING NCS GROUPS

$MnHg(SCN)_4$	278 s, br, 213 m, br
$FeHg(SCN)_4$	296 s, 256 m, 216 m
$CoHg(SCN)_4$	303 s, ~276 sh, 219 m
$NiHg(SCN)_4$	303 m, ~250 s, v br
$CuHg(SCN)_4$	318 s, 282 vs, ~266 sh, w
$ZnHg(SCN)_4$	327 s, ~250 sh, 217 m
$CoCd(SCN)_4$	303 vs, 276 sh, 230 m

As well as the bands discussed above the compounds $MHg(SCN)_4$, M = Mn, Fe, Co, Zn, showed a band of medium intensity at 213–219 cm.$^{-1}$, and in the spectrum of $CoCd(SCN)_4$ there was a similar band at 230 cm.$^{-1}$. We tentatively assign these as Hg–S and Cd–S stretching absorptions, respectively. If these assignments are correct, it is likely that the absorption at 213–219 cm.$^{-1}$ for $MHg(SCN)_4$ represents only an upper component of a split Hg–S stretching band since our studies on $M(SCN)_x^{n-}$ ions suggested that the Hg–S stretching frequency of $Hg(SCN)_4^{2-}$ lies below 200 cm.$^{-1}$. However, in the absence of data below 200 cm.$^{-1}$ for $Hg(SCN)_4^{2-}$ and $Cd(SCN)_4^{2-}$ we cannot be certain that the 200–230 cm.$^{-1}$ bands discussed above do not arise from deformation modes.

The structure of $CuHg(NCS)_4$ is quite different[12] from that of $CoHg(SCN)_4$. The copper ion is surrounded by a rectangle of nitrogen atoms (two at 1.94 Å. and two at 1.85 Å.) with two sulfur atoms in approximately axial positions at 3.00 Å. This difference in structure is reflected in the infrared spectrum. The two strong bands at 318 and 282 cm.$^{-1}$ may be assigned as the two Cu–N stretches expected for a $Cu-N_4$ group with D_{2h} symmetry. For this compound there was no absorption corresponding to the band of medium intensity found at 219 cm.$^{-1}$ for $CoHg(SCN)_4$. However in $CuHg(SCN)_4$ the $Hg-S_4$ tetrahedron is quite severely distorted[12] and the Cu-S bond is probably quite weak.

The exact structure of $NiHg(SCN)_4$ is not known. However, electronic spectral and magnetic studies[4]

---

[13] D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, **19**, 925 (1963).

[14] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

[15] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *ibid.*, 2189 (1963).

[16] J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).

[17] J. W. Jeffery, *Nature*, **159**, 610 (1947); *Acta Cryst., Suppl.*, A66, abstract 6.6 (1963).

[18] W. Stahl and M. Straumanis, *Z. physik. Chem.*, **193**, 121 (1943).

suggest the presence of a tetragonal ligand field around the nickel ion essentially similar to that in the olive-yellow form of $[(C_6H_5)_4As]_2Ni(NCS)_4$ discussed earlier. In agreement with this, the infrared spectra of these two compounds in the range 400–200 cm.$^{-1}$ are rather similar. The spectrum of $NiHg(SCN)_4$ shows one relatively sharp band at 303 cm.$^{-1}$ and broad, ill-resolved absorption from ~280 to 200 cm.$^{-1}$ with a maximum at ~250 cm.$^{-1}$.

Conclusions.—The results of our studies suggest that a distinction between N- and S-bonded thiocyanate groups can be made from their infrared spectra in the region 400–200 cm.$^{-1}$. Isothiocyanate complexes give rise to strong bands at values slightly above the M–Cl stretches of the corresponding chloro complexes (assuming the same symmetry). Thiocyanato complexes, on the other hand, give bands of medium intensity which, in the cases studied here, fall approximately midway between the metal–halogen stretches of the corresponding chloro and bromo complexes.

Acknowledgment.—We thank the D.S.I.R. for a Research Studentship (to D. F.) and Professor R. S. Nyholm, F.R.S., for the use of the Grubb-Parsons DM.2 spectrometer.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH

Thermodynamics of Metal Cyanide Coordination. IV. Log $\beta_i°$, $\Delta H_i°$, and $\Delta S_i°$ Values for the Zinc(II)–Cyanide System at 25°[1a]

BY REED M. IZATT,[1b] JAMES J. CHRISTENSEN,[1b] JAMES W. HANSEN, AND GERALD D. WATT[1c]

Received July 13, 1964

A pH titration study of the Zn^{2+}–CN^- system at 25° in dilute aqueous solution provides positive evidence for only $Zn(CN)_2$(aq), $Zn(CN)_3^-$, and $Zn(CN)_4^{2-}$ up to an 8:1 total cyanide to zinc ratio. Use of an IBM 7040 digital computer has allowed extensive analysis of the pH titration data to be carried out with the only major assumption being that of the species present. The absence of the $ZnCN^+$ species is substantiated by a polarographic study of the system. Equilibrium constants valid at ionic strength values of 0, 3.5×10^{-3}, and 7×10^{-3} are reported for the formation at 25° of each of the above species from Zn^{2+} and CN^-. Calorimetric $\Delta H_i°$ values are also reported together with $\Delta S_i°$ values. Preferential occurrence of certain complexes is discussed in the light of these thermodynamic quantities.

Introduction

Metal–cyanide complexes have occupied an important place in the development of our understanding of transition metal chemistry. One interesting, although as yet little understood, fact about these complexes is that some, *e.g.*, $Hg(CN)_4^{2-}$,[2,3] are formed in a stepwise fashion by interaction of CN^- with the metal ion while others are not. For example, in the $Ni(CN)_4^{2-}$ system[4] measurable concentrations of intermediate metal–cyanide species apparently do not exist even at low CN^- to Ni^{2+} ratios. Because of the opposite behavior of CN^- toward Ni^{2+} and Hg^{2+}, it seemed to us that the next logical step would be a study of the Zn^{2+}–CN^- system. In common with nickel and mercury, zinc has the oxidation state +2. In addition, both Zn^{2+} and Ni^{2+} are in the same period differing in that they are d^{10} and d^8 ions, respectively. Also, Zn^{2+} resembles Hg^{2+} in being a d^{10} ion; however, the underlying energy levels of these metal ions differ considerably. In view of these similarities and differences it appeared to be of interest to learn which, if either, of these M^{2+}–CN^- systems the Zn^{2+}–CN^- system resembled. Also, thermodynamic data for a large number of metal–CN^- systems should provide the basis for a better understanding of the nature of the bonding forces and, consequently, of stepwise and nonstepwise behavior in these systems.

Published data for the Zn^{2+}–CN^- system are not consistent either with respect to which cyanide complexes intermediate between Zn^{2+} and $Zn(CN)_6^{4-}$ exist, or to the magnitude of β_4[5] for the formation of $Zn(CN)_4^{2-}$. Log β_4 values ranging from 16 to 21.4 have been reported,[6–9] while the values reported for log β_3[7–10] and log β_5[8] lie within the range of these reported log β_4 values. Kunschert[10] and Ferrell, Ridgion, and Riley[11] report that both Zn and Zn–Hg electrodes are attacked by aqueous CN^- solutions. Since most previous work on the Zn^{2+}–CN^- system has been done

---

(1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(04-3)-299. Presented at the 19th Annual Northwest Regional American Chemical Society Meeting, Spokane, Wash., June 15–16, 1964. (b) To whom inquiries should be directed. (c) Supported by a Public Health Service predoctoral fellowship (No. GM 20, 545) from the Division of Research Grants, Public Health Service.

(2) L. Newman, J. de O. Cabral, and P. N. Hume, *J. Am. Chem. Soc.*, **80**, 1814 (1958).

(3) R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, **20**, 19 (1961).

(4) J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, **2**, 337 (1963).

(5) $\beta_i = [Zn(CN)_i^{2-i}]/[Zn^{2+}][CN^-]^i$; corresponding equilibrium constants valid at zero ionic strength are designated $\beta_i°$.

(6) H. Euler, *Ber.*, **36**, 3400 (1903).

(7) K. Masaki, *Bull. Chem. Soc. Japan*, **6**, 89 (1931).

(8) I. Pines, *Collection Czech. Chem. Commun.*, **1**, 429 (1929).

(9) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1940 (1932).

(10) F. Kunschert, *Z. anorg. Chem.*, **41**, 337 (1904).

(11) E. Ferrell, J. M. Ridgion, and H. L. Riley, *J. Chem. Soc.*, 1121 (1936).