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A Study of Transition Metal Compounds Containing the Tricyanomethanide Ion

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The physical properties of five transition metal tricyanomethanide compounds of the type $M[C(CN)_3]_2 \cdot xH_2O$ (M = Mn, Fe, Co, Ni, Cu) have been investigated in an attempt to deduce the coordination symmetry of the cations and the structure of the anion in these salts. Magnetic and ligand field spectral results are strongly suggestive of weak field approximately octahedral coordination in each case. The infrared results indicate cation–anion interaction through nitrogen producing a site symmetry lower than the intrinsic D_{3h} symmetry of the free anion, but cannot be interpreted in terms of a significant distortion of the anion from planarity. A polymeric structure is proposed which is consistent with the spectral results and insolubility of these compounds. The nonlinear structure of the dicyanoamide ion, $N(CN)_2^-$, is confirmed by Raman spectroscopy. The electronic structures of $C(CN)_3^-$ and $N(CN)_2^-$ have been investigated using the extended Hückel theory.

Introduction

In recent years a number of cyanohydrocarbons have been prepared[2-4] and many of these have been shown to be unusually strong acids with strengths comparable to those of the mineral acids.[5] The remarkable ease of proton loss is undoubtedly due to the large resonance stabilization of the conjugate base cyanocarbon anions, many of which are known to form stable salts with organic and metallic cations.[2-4] A number of cyanocarbon compounds containing the divalent ions of the first transition series have been isolated.[3,4]

The manner in which transition metal ions might interact with or be coordinated by cyanocarbon anions is not clear. These anions possess as formal coordinating sites only the weakly basic nitrile group and in general do not have favorable geometries for chelate ring formation. In this work we have attempted to provide at least a partial clarification of the interaction of a given cyanocarbon anion with a series of divalent transition metal ions in the solid phase. We have chosen to study the compounds of the simplest cyanocarbon anion, the tricyanomethanide ion,[2a,4] $C(CN)_3^-$, and report the results of an examination of those spectral and magnetic properties which should be indicative of the approximate symmetry of the coordination spheres of the cations and of the mode of cation–anion interaction. In addition, the results of a complete molecular orbital calculation on $C(CN)_3^-$ are reported as are further spectral results on the related dicyanoamide ion, $N(CN)_2^-$.

Experimental[6]

Preparation of Compounds.—Potassium tricyanomethanide was prepared as previously described[4] and was obtained as a completely white crystalline solid by one recrystallization from water followed by one recrystallization from acetonitrile. Salts of divalent metal ions were precipitated from ~50 ml. of hot aqueous solution prepared by mixing ~25-ml. solutions containing 0.025 mole of metal chloride or sulfate and 0.050 mole of $KC(CN)_3$.[4] All compounds are too insoluble to be recrystallized from water and are in general insoluble in polar organic solvents except for dimethylformamide and dimethyl sulfoxide. The precipitated products were washed well with water, dried to constant weight *in vacuo* at 100°, and then analyzed.

$Mn[C(CN)_3]_2 \cdot {}^1/_4H_2O$.—White crystals. *Anal.* Calcd.: C, 40.12; H, 0.21; Mn, 22.94; N, 35.10. Found: C, 39.96; H, 0.03; Mn, 23.04; N, 33.02.

$Fe[C(CN)_3]_2 \cdot {}^1/_2H_2O$.—The pale green solid which precipitated became light yellow on drying. *Anal.* Calcd.: C, 39.22; H, 0.41; Fe, 22.80; N, 34.30. Found: C, 38.84; H, 0.35; Fe, 23.0; N, 33.53.

$Co[C(CN)_3]_2 \cdot {}^1/_2H_2O$.—Orange microcrystals. *Anal.* Calcd.: C, 38.73; H, 0.40; Co, 23.76; N, 33.88. Found (first preparation): C, 39.02; H, 0.63; Co, 23.66; N, 32.96; (second preparation): C, 38.41; H, 0.51; Co, 23.17.

$Ni[C(CN)_3]_2 \cdot xH_2O$.—The pale blue precipitate became yellow-green on drying. The dried form was extremely hygroscopic and rapidly turned light green on exposure to air. Both the yellow-green and light green forms are evidently hydrated but differ only slightly in the degree of hydration which is established by analysis to be $0 < x \leq {}^1/_2$. *Anal.* Calcd. for $x = {}^1/_2$: C, 38.77; H, 0.40; Ni, 23.69; N, 33.91. Calcd. for $x = 0$: C, 40.23; H, 0.00; Ni, 24.58; N, 35.19. Found (yellow-green form): C, 38.79; H, 0.34; Ni, 24.44; N, 34.21; (light green form): C, 38.53; H, 0.15; Ni, 23.58; N, 33.79; (pale blue form): Ni, 23.45.

$Cu[C(CN)_3]_2 \cdot {}^1/_4H_2O$.—Brown crystals. *Anal.* Calcd.: C, 38.71; H, 0.20; Cu, 25.60; N, 33.87. Found: C, 38.81; H, 0.42; Cu, 25.60; N, 33.05.

Physical Measurements.—Visible and near-infrared spectra were taken with a Cary Model 14 spectrophotometer. Transmittance spectra of solids were studied using finely dispersed hydrocarbon oil mulls sandwiched between quartz plates. Conductivities were measured on a Serfass conductivity bridge. Infrared spectra were obtained on Nujol or hexachlorobutadiene mulls using a Cary–White Model 90 spectrometer capable of *ca.* ±1 cm.$^{-1}$ resolution in the 2500–450 cm.$^{-1}$ range. Raman spectra were recorded on aqueous solutions using a Cary Model 81 photoelectric spectrometer with Hg 4358 Å. excitation. Magnetic measurements were made by the Gouy method using an aqueous nickel chloride solution as the calibrant.

(1) National Science Foundation Predoctoral Fellow, 1962–present.

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(3) W. J. Middleton, E. L. Little, D. D. Coffman, and V. Engelhart, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(4) S. Trofimenko, E. L. Little, and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962).

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Results and Discussion

This work deals with compounds of the type $M[C(CN)_3]_2 \cdot xH_2O$ in which M = Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, and Cu^{+2}. These compounds have been previously prepared by Trofimenko, *et al.*,[4] who established the water content by metal analysis only. Our samples, which were prepared in the same way but then dried to constant weight *in vacuo* at 100°, have been completely analyzed. In all cases the analyses, together with the appearance of a weak broad infrared absorption at ~1630 $cm.^{-1}$ (Nujol mull), indicate the presence of a small amount of water in the dried samples. The water content has been inferred principally from the metal and carbon analyses[7] and cannot be regarded as definite. However, an examination of the analytical results does allow the conclusion that $x \leqslant 1/2$. In this respect our results differ from those of Trofimenko, *et al.*,[4] only in their formulation of the manganous and cupric compounds as anhydrous. The nickel compound has been obtained in three visually distinguishable forms, pale blue, yellow-green, and light green, which apparently are hydrated to slightly different extents. The pale blue (undried) form corresponds to the nickel species obtained previously.[4]

Electronic Structure of $C(CN)_3^-$.—The structure of the tricyanomethanide ion has been established on the basis of preliminary X-ray results to be planar with D_{3h} symmetry.[8] The electronic structure of this ion has been investigated using the recently developed extended Hückel theory.[9] The Hückel theory in this form includes overlap and all interactions so that all off-diagonal terms in the energy, H_{ij}, and S_{ij} are retained. The calculations were performed using H_{ii} (N2s) = −26.00, H_{ii} (N2p) = −13.40 e.v., and the H_{ii} (C2s, 2p) values given previously.[9] The matrix elements H_{ij} were approximated as described.[9] Slater exponents were taken from the tabulation of Clementi and Raimondi,[10] and all calculations were carried out using atomic coordinates derived from the X-ray results.[8]

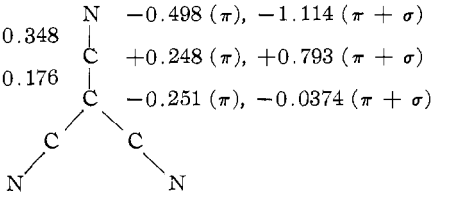
Certain pertinent results of the calculations are set out in Table I. The seven π-molecular orbitals transform as a_2'' or e'' in D_{3h} symmetry. Our results, which include calculations of both π- and σ-MO energies, show the highest filled orbital to be the nonbonding $\pi(a_2'')$ orbital. Listed are the energies of all π-MO's and those σ-MO's which fall between the most excited π-MO and $\pi(a_2'')$. The π-electronic structure is obviously $(a_2'')^2(e'')^4(a_2'')^2$. The electronic spectrum of an aqueous solution of $C(CN)_3^-$ has been recorded previously,[3,11] and in the experimentally accessible ultraviolet region only the band at 47,400 $cm.^{-1}$ (ϵ 37,400) has been observed. For this highly allowed transition the only reasonable assignment is $^1A_1[(a_2'')^2] \rightarrow {}^1E'[(a_2'')(e'')]$. The results of the charge density and total π-overlap population[12] calculations reveal the significant delocalization implied by the observed C–C distance of 1.40 Å.,[8] as do the π-bond orders (C–C 0.524, C–N 0.751) calculated from the simple Hückel theory. The charge density results show that each nitrogen is considerably more negative than the central carbon, in terms of both π-electron charge distribution and net ($\pi + \sigma$) charge. The π-charge distribution is similar to those calculated for two larger cyanocarbon anions using the simple Hückel theory.[13] On the basis of charge distribution nitrogen is the most likely site of electrophilic attachment. The site of protonation of $C(CN)_3^-$ in solution is unknown, but the free acid as isolated from aquoethereal solution is claimed to be dicyanoketeneimine rather than simple cyanoform, $HC(CN)_3$.[14]

TABLE I

MOLECULAR ORBITAL CALCULATIONS ON $C(CN)_3^-$

Orbital	Energy, e.v.
$\pi^*(a_2'')$	−2.696
$\sigma^*(a_2')$	−6.338
$\pi^*(e'')$	−7.508
$\sigma^*(e')$	−7.585
$\pi(a_2'')$	−12.252
$\pi(e'')$	−14.746
$\pi(a_2'')$	−15.329

Charge Densities and Total π-Overlap Populations[a]



[a] Signed quantities are the charge densities, unsigned quantities the overlap populations.

Electronic Spectra.—The spectra of all compounds were obtained as transmittance spectra of solids in finely dispersed hydrocarbon mulls. Solution spectra of the intact compounds could not be measured due to extensive, if not complete, dissociation in those two solvents (DMSO, DMF) in which the compounds would dissolve. Measured conductivities in DMF solution (*cf.* Table II) indicate the presence of 2:1 electrolytes. The visible spectra of DMF solutions are identical with those reported for $M(DMF)_6^{+2}$.[15,16] The spectrum of $Co[C(CN)_3]_2$ in DMF remained unchanged even when the mole ratio $C(CN)_3^-/Co$ was as large as 75:1 (2.76 *M*:0.037 *M*). This observation proves that $C(CN)_3^-$ is a much weaker ligand than Cl^- with respect to Co(II), and probably generally, inasmuch as $CoCl_2$ in the same solvent (with no added chloride) exists in the forms of octahedral and tetrahedral chloride-containing species.[17]

A detailed consideration of the transmittance spec-

(7) Nitrogen microanalyses gave consistently low results for $x \leqslant 1/2$ (see Experimental section).

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(9) For detailed explanation and applications of the extended Hückel theory, see R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480 (1964).

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(11) R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

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(14) S. Trofimenko, *J. Org. Chem.*, **28**, 217 (1963).

(15) W. Schneider, *Helv. Chim. Acta*, **46**, 1842 (1963).

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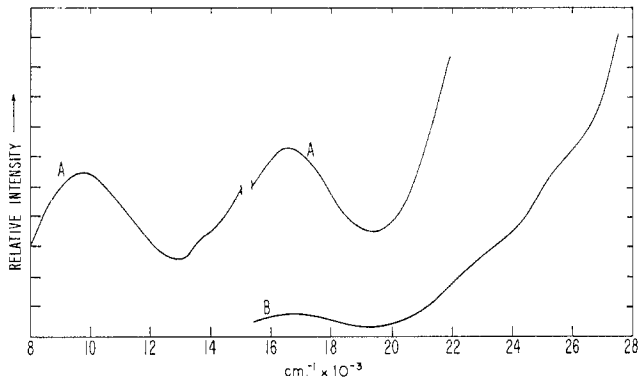

Fig. 1.—Transmittance spectrum of $Ni[C(CN)_3]_2$ (light green form) in a hydrocarbon mull: A, thick mull; B, dilute mull.

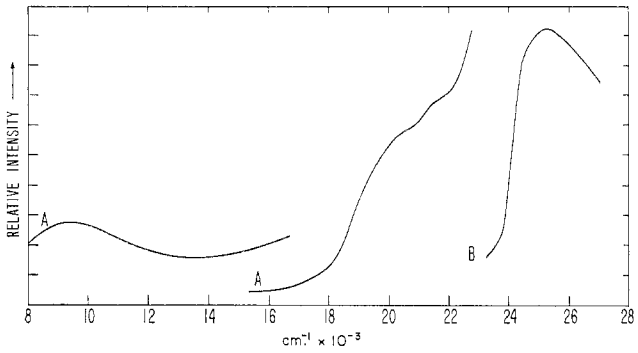

Fig. 2.—Transmittance spectrum of $Co[C(CN)_3]_2 \cdot {}^1/_2H_2O$ in a hydrocarbon mull: A, thick mull; B, dilute mull.

TABLE II
CONDUCTIVITIES AND MAGNETIC MOMENTS[a]

Compound	Λ[b]	μ_{eff}, B.M.[c]
$Mn[C(CN)_3]_2 \cdot {}^1/_2H_2O$	149	5.93
$Fe[C(CN)_3]_2 \cdot {}^1/_2H_2O$	138	5.17
$Co[C(CN)_3]_2 \cdot {}^1/_2H_2O$	137	4.79
$Ni[C(CN)_3]_2$ (pale blue)	...	3.20
$Ni[C(CN)_3]_2$ (light green)	...	3.15
$Ni[C(CN)_3]_2$ (yellow-green)	136	3.18
$Cu[C(CN)_3]_2 \cdot {}^1/_4H_2O$	156	1.86
$Co(NO_3)_2 \cdot 6H_2O$	143	...
$KC(CN)_3$	76	...

[a] Measurements made at ambient room temperature (23–26°). [b] Cm.² equiv.$^{-1}$ ohm^{-1} in $\sim 10^{-3}$ M solutions prepared from Spectro grade dimethylformamide. [c] Calculated from the Curie law.

pounds are most informative and are given in Fig. 1 and 2. The magnetic data (*cf.* Table II) show all compounds to be high spin and are consistent with those found for octahedral complexes.

The spectra of two visually distinct forms of $Ni[C(CN)_3]_2$ are given in Table III. They differ insignificantly except for the failure to observe the weak band at $\sim$22,600 cm.$^{-1}$ in the blue form. Taking Dq as 950–970 cm.$^{-1}$ the spectra can be fit most satisfactorily to the Liehr–Ballhausen nomograph[18] calculated for rigorously octahedral Ni(II) using $\lambda = -275$ cm.$^{-1}$, $F_2 = 14F_4$, $F_4 = 90$ cm.$^{-1}$. The assignments for these and other spectra are given in the notation for octahedral symmetry, but this is meant to imply only that the *apparent* symmetry is pseudo-octahedral. The

TABLE III
ELECTRONIC SPECTRA OF $M[C(CN)_3]_2$ COMPOUNDS

		λ_{max}, cm.$^{-1}$		
			Obsd.	
Compound	Assignment	Calcd.	Light green form	Blue form
$Ni[C(CN)_3]_2$	$^3A_{2g} \rightarrow {}^3T_{2g}$	9,700	9,700 (w)	9,500 (w)
	$^3A_{2g} \rightarrow {}^1E_g$	12,500	$\sim$13,800 (sh, vw)	$\sim$13,800 (sh, vw)
	$^3A_{2g} \rightarrow {}^3T_{1g}$	15,300 16,600	16,700 (w)	16,500 (w)
	$^3A_{2g} \rightarrow {}^1A_{1g}$	20,900	$\sim$22,600 (sh, w)	...
	$^3A_{2g} \rightarrow {}^1T_{2g}$	22,600		
	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	25,900	$\sim$25,500 (sh, w)	$\sim$26,000 (sh, w)
$Co[C(CN)_3]_2 \cdot {}^1/_2H_2O$	$^4T_{1g} \rightarrow {}^4T_{2g}$	9,500	9,600 (w)	
	$^4T_{1g} \rightarrow {}^4A_{2g}$	20,300	$\sim$20,000 (sh, w)	
	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	22,800	$\sim$21,300 (sh, w)	
	Charge transfer	...	25,000 (s)	
$Fe[C(CN)_3]_2 \cdot {}^1/_2H_2O$	$^5T_{2g} \rightarrow {}^5E_g$	...	12,100 (w)	
$Cu[C(CN)_3]_2 \cdot {}^1/_2H_2O$	$^2E_g \rightarrow {}^2T_{2g}$	...	13,900 (w)	
	Charge transfer	...	21,800 (s)	

tra is not in order in view of their necessarily limited quality and the uncertainty in the symmetry environments of the metal ions. The observed spectral features are set out in Table III. All bands of interest are weak and in several cases some of these can be detected only as shoulders superimposed on steeply rising contours which originate from charge-transfer bands and increased scattering of radiation at the higher frequencies. We wish only to point out that the observable features of these spectra are highly suggestive of approximate octahedral symmetry at the metal ion positions. In this connection the spectra of the nickel and cobalt complexes spectrum of $Co[C(CN)_3]_2$ is in satisfactory agreement with expectation for an octahedral complex based on the Orgel diagram[19] assuming $Dq \sim 1100$ cm.$^{-1}$. The spectra of the Cu(II) and Fe(II) compounds exhibit single broad bands with no discernible splitting. The spectrum of $Mn[C(CN)_3]_2$ could not be obtained because of the low intensities of the spin-forbidden transitions. Comparison of band energies and Dq values with those from recent tabulations for octahedral Co,

(18) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).
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TABLE IV
INFRARED SPECTRA OF $M[C(CN)_3]_2$ COMPOUNDS[a]

$KC(CN)_3$ Raman (H_2O)[b]	$KC(CN)_3$ Infrared (solid)[c]	Assignment[d]	Mn	Fe	Co	Ni	Cu
	404* w	ν_5, a_2''					
483 (2) dp	479*, 486* w	ν_9 (ν_{10}?), e'	477 vw	478, 484 vw	476, 484 vw	474, 482 vw	475 vw
	569 vs	ν_4, a_2''	563, 566 s	565, 568 s	563, 566 s	559, 563 s	558, 562 s
609 (2) dp	608 vw	ν_8, e'	614 m	614 w	615 m	616 w	615 m
657 (5) p	655* vw	ν_2, a_1'					
973 (1) p	972 vw	$2\nu_9$	949, 961 vw	951, 965 vw	948, 963 vw	945, 962 vw	945, 970 vw
	1018 vw	$\nu_5 + \nu_8$(?)[e]	1030 vs	1032 vs	1042 vw	1040 vw	1030 vw
1243 (3) dp	1240, 1253 m	ν_7, e'	1255, 1265 m	1254, 1265 m	1254, 1269 s	1250, 1270 m	1261, 1268 m
	1273 w	$\nu_8 + \nu_2$					
		HOH bend, water	1630 b, vw	1620 b, m	1630 b, m	1640 b, w	1620 b, w
	1908, 1938 w	$2\nu_2 + \nu_8$(?)					
	2130 vw	ν_6, $^{13}C{\equiv}N$ / $\nu_5 + \nu_7 + \nu_4$(?)	2158, 2165 vw	2156 vw	2156 vw, 2171 sh	2164, 2179 sh, vw	2159 sh, 2177 vw
2173 (10) dp	2178 vs, 2193 sh	ν_6, e'	2197, 2210 vs, sh	2196, 2210 vs, sh	2198, 2218 vs, m	2209, 2227 vs, m	2205, 2221 vs, m
2225 (10) p	2215 vvw	ν_1, a_2'	2257 w	2246 vw	2263 w	2269 w	2271 m

[a] s, strong; m, medium; w, weak; vs, very strong, etc., sh, shoulder; b, broad. [b] Data from ref. 24; dp, depolarized; p, polarized; relative intensities in parentheses. [c] Frequencies denoted with asterisk from ref. 24, all others are from this work. [d] For description of vibrational modes see ref. 24. [e] Combination should not be active in infrared, a possible alternative is $\nu_2 + \nu_5$.

Cu, Ni,[20] and Fe[21] complexes shows that the ligand field splittings are considerably greater than those for $M-O_6$ type complexes and are quite comparable with those for $M(NH_3)_6^{+2}$. A further and more pertinent comparison can be made with spectral data for $M(CH_3CN)_6^{+2}$ complexes,[22] from which it can be inferred that Dq(Ni) = 1050 cm.$^{-1}$ and Dq(Co) ~1100 cm.$^{-1}$. These results strongly suggest that the small amount of water present in the crystalline tricyanomethanide compounds has no significant effect on the ligand field strengths, which are effectively nearly the same as those produced by coordination of six simple nitrile molecules.

Infrared Spectra.—The vibrational spectrum of $KC(CN)_3$ has been reported previously[23,24] and can be interpreted in terms of the D_{3h} structure of the anion. Miller and Baer[24] have presented a nearly complete analysis of the infrared and Raman spectra and our interpretations are in substantial agreement with theirs. We have examined mull spectra of the transition metal tricyanomethanide compounds in the 4000–450 cm.$^{-1}$ range under conditions of high resolution. Frequencies in the range 2300–450 cm.$^{-1}$ are set out in Table IV; included for comparison purposes are infrared and Raman data for $KC(CN)_3$.[24] Only very weak absorptions occur above 2300 cm.$^{-1}$ and these can be satisfactorily assigned as overtone or combination frequencies.

Infrared selection rules for the possible effective symmetries of $C(CN)_3^-$ in the metal compounds are given in Table V. Cases in which the dominant symmetry of the anion itself is C_{2v} or C_s can be discarded. The strong similarity between the spectrum of $C(CN)_3^-$ in its potassium salt and the spectra in the transition metal compounds provides convincing evidence that the planar (D_{3h}) structure of the ion is not significantly degraded in the latter compounds. Departures from rigorous D_{3h} symmetry are apparent from the spectra in all cases, however, and are reflected in the previously noted splittings[23,24] of several of the skeletal e' vibrations in solid $KC(CN)_3$. This effect can now be interpreted from the preliminary X-ray results[8] which reveal that the site symmetry of the anion can be no higher than C_{2v}. Similar splittings are also observed in the transition metal salts for which suggested assignments of all observable fundamentals are given in Table IV.

TABLE V
INFRARED SELECTION RULES FOR $C(CN)_3^-$

Symmetry	Fundamentals	C≡N Stretches
D_{3h}	$2a_2'' + 4e'$	e'
C_{3v}	$4a_1 + 5e$	$a_1 + e$
C_{2v}	$6a_1 + 3b_1 + 5b_2$	$2a_1 + b_2$
C_s	$9a' + 6a''$	$2a' + a''$

In an attempt to provide a further assessment of the departure of $C(CN)_3^-$ and/or its environment from D_{3h} symmetry high resolution spectra in the C≡N stretching region have been examined and three representative spectra appear in Fig. 3. In every case four or five absorptions of widely varying intensities are apparent. The assignment of the most intense feature as ν_6 (or one component thereof) is obvious; its in-

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(24) F. A. Miller and W. K. Baer, *Spectrochim. Acta*, **19**, 73 (1963).

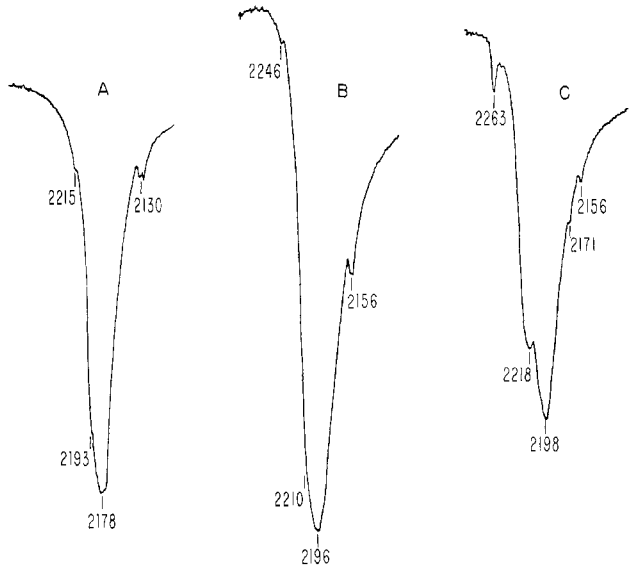


Fig. 3.—Infrared spectra of tricyanomethanide compounds in the C≡N stretching region (hydrocarbon mulls): A, $KC(CN)_3$; B, $Fe[C(CN)_3]_2 \cdot {}^1/_2H_2O$; C, $Co[C(CN)_3]_2 \cdot {}^1/_2H_2O$.

creased frequency in the transition metal salts compared to $KC(CN)_3$ is a strong indication of enhanced interaction between the nitrogen of the cyano groups and the cations[25] and is explicable using a simple kinematic model.[26] A shoulder or distinct band is observed on the immediate high frequency side of the most intense feature of the transition metal salts. A shoulder is also observed in solid $KC(CN)_3$ but is not present in aqueous solution. Thus, it is concluded that in all cases the band or shoulder is the other component of $\nu_6(e')$ which arises because of the lower site symmetry in the solid. This feature is most pronounced in those compounds (Cu, Ni, Co) in which the cation in general forms the most tightly bound complexes whereas in the other cases (Mn, Fe) only a shoulder is observed. Additional infrared evidence for the degradation of the D_{3h} symmetry of the anion in the transition metal salts arises from a single relatively weak band occurring in the range 2246–2271 cm.$^{-1}$. The intensities and frequencies of this feature rule out assignment as a combination band. The most reasonable assignment is that of the totally symmetric ν_1 (a'_1) C≡N stretch, infrared silent in D_{3h} symmetry, which has become weakly allowed. The very weak 2215 cm.$^{-1}$ absorption in $KC(CN)_3$ might be assigned similarly. The very weak bands on the low-energy side of the most intense feature are perhaps most reasonably assigned as $^{13}C \equiv N$ stretches, but it is noted that the allowed combination bands $\nu_7 + \nu_4 + \nu_5$ and $2\nu_9 + \nu_7$ might also appear in this region. In summary, the infrared results show that in the transition metal salts the tricyanomethanide ion and/or its immediate environment does not possess rigorous D_{3h} symmetry. All spectral features when considered collectively are incompatible with a significantly nonplanar entity such as is found in $ClC(CN)_3$.[24] It is concluded that the intrinsic D_{3h} symmetry of the anion is retained and that the arrangement of cations about the anion produces a lower site symmetry and concomitant splittings of the e′ vibrations.

(25) H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958); W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960); B. J. Hathaway and A. E. Underhill, *ibid.*, 3091 (1961); B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *ibid.*, 3215 (1961); M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *ibid.*, 5665 (1963); S. C. Jain and R. Rivest, *Can. J. Chem.*, **41**, 2130 (1963).

(26) Treating the M—N≡C grouping as a linear three-body oscillator[27] and taking the C≡N force constant in $C(CN)_3^-$ as 18.23 mdynes/Å,[28] it can be shown that a purely kinematic effect would tend to raise the C≡N frequencies by 20–40 cm.$^{-1}$ for K_{MN} values in the range 0.8–2.3 mdynes/Å.

(27) G. M. Barrow, "Introduction to Molecular Spectroscopy," McGraw-Hill Book Co., New York, N. Y., 1962, pp. 208–212.

(28) G. Nagarajan, *Indian J. Pure Appl. Phys.*, **1**, 273 (1963).

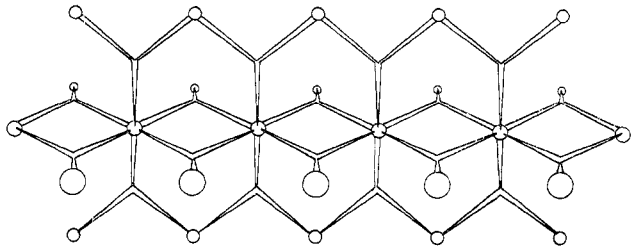


Fig. 4.—Proposed structure for $M[C(CN)_3]_2$ compounds: O, M^{+2}; λ, $C(CN)_3^-$.

The proposed structure of the transition metal tricyanomethanide compounds which is consistent with all spectral results is shown in Fig. 4. A regular structure is assumed and consists of intersecting planes of $C(CN)_3^-$ ions with divalent cations occupying pseudo-octahedral holes. Each cation is coordinated by six nitrogens with the true symmetry about the metal being D_{2h}. The site symmetry of $C(CN)_3^-$ can be no higher than C_{2v}, but surely is not far from D_{3h}. This polymeric model is also consistent with the insolubility of the compounds in all but extremely polar strongly coordinating solvents, but does not take into account the small amounts of water present.

Dicyanoamide Ion.—In connection with our studies of the tricyanomethanide ion, we have also investigated the dicyanoamide ion in order to establish its structure. Extended Hückel-type molecular orbital calculations of the total orbital energy[9] as a function of the C–N–C angle give an energy difference of only ~0.9 e.v. between the 180° ($D_{\infty h}$) and 110° (C_{2v}) structures,[29] with the former more stable. While no strict reliance can be placed on these computed energies, the implication is that there might be a small energy difference between the linear and bent forms. Previously Kuhn and Mecke,[30] and later Sprague, *et al.*,[31] had inferred a bent structure from the observation of two infrared-active C≡N stretches, $a_1 + b_1$, at 2179 and 2232 cm.$^{-1}$, respectively. To confirm the bent structure for $N(CN)^{2-}$ we have examined the infrared and Raman spectra of this ion in aqueous solution with these results in the C≡N region (cm.$^{-1}$): 2150 m and 2212 vs (Raman, ρ = 0.78, 0.33, respectively), 2151 vs and 2211 m (infrared). The second Raman band is definitely polarized and is assigned to the a_1

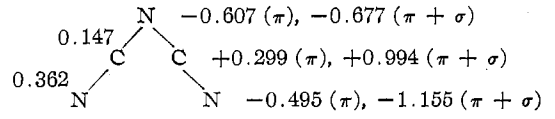
(29) Calculations were made for 180, 160, 120, and 110° angles using the same parameters as for $C(CN)_3^-$ including $d_{C\equiv N}$ = 1.15, d_{N-C} = 1.35 Å.

(30) M. Kuhn and R. Mecke, *Ber.*, **94**, 3010 (1961).

(31) J. W. Sprague, J. G. Grasselli, and W. M. Ritchey, *J. Phys. Chem.*, **68**, 431 (1964).

mode, whereas the first band is very probably depolarized and is assigned to the b_1 mode. Thus, the bent structure of the ion in the solid and in solution is confirmed, but the assignment of the stretching modes by Kuhn and Mecke is reversed. A recent infrared and Raman analysis of $S(CN)_2$,[32] which is isomorphous with bent $Se(CN)_2$,[33] has yielded $\nu_{C\equiv N}$ $(a_1) > \nu_{C\equiv N}$ (b_1).

The results of molecular orbital calculations of the charge densities and overlap populations for nonlinear $N(CN)_2^-$ follow. The signed quantities are the charge densities, the unsigned quantities the total π-overlap populations. These results refer to $\angle C\text{–}N\text{–}C = 120°$,



(32) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1731 (1963); see also E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J. Chem. Soc.*, 704 (1964).

(33) A. C. Hazell, *Acta Cryst.*, **16**, 843 (1963).

but show only minor variations from 110 to 160°. The charge distribution strongly resembles that in $C(CN)_3^-$ with the terminal nitrogens being the more negative. That these atoms interact with coordinating cations is evident from the increase in the C≡N stretching frequencies in copper, mercury, and lead salts compared to $NaN(CN)_2$.[30,34]

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(34) NOTE ADDED IN PROOF.—A very recent and more complete X-ray study than that reported in ref. 8 has shown that in $NH_4C(CN)_3$ the anion is slightly nonplanar with the central carbon 0.13 Å. above the plane of the three nitrogens [C. Bugg, R. Desiderato, and R. L. Sass, *J. Am. Chem. Soc.*, **86**, 3157 (1964)]. In the transition metal salts a similar distortion and/or site symmetry effects could account for some of the infrared results. The conclusion that the structure of the anion in these salts and in $KC(CN)_3$ is essentially the same is unaffected.

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Identification of the Geometrical Isomers of Some Tris-Chelate Cobalt(III) Complexes by Nuclear Resonance

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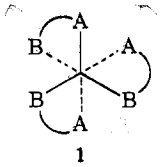
The proton resonance spectra of tris-(N-R-salicylaldimine) Co(III) complexes (R = methyl, ethyl, *p*-tolyl) and a new series of tris-(N-R-pyrrole-2-aldimine) Co(III) complexes (R = methyl, ethyl, isopropyl, *sec*-butyl) have been examined. The spectra provide unequivocal evidence for the existence of the *trans* isomer. In no case was any *cis* isomer detected. The apparent exclusive formation of the *trans* isomer is ascribed to significantly reduced steric interactions among the nitrogen substituents compared to the *cis* configuration. The more general formation of octahedral complexes in the pyrrole-2-aldimine than in the salicylaldimine series is concluded to be due to somewhat reduced steric interactions among these substituents. A general preparative method for tris(pyrrole-2-aldimine) Co(III) complexes is given.

Introduction

Tris-chelate metal complexes containing three identical unsymmetrical bidentate ligands can exist in two geometrically isomeric configurations, *cis* and *trans*. This type of isomerism is well recognized and the isomers have in some cases been identified by their ligand field spectra,[2-4] with a particular example being tris(glycinato)cobalt(III).[2] More recently, Fay and Piper[5-7] have separated *cis* and *trans* isomers of unsymmetrical β-diketones and have identified each by nuclear resonance. The *cis* isomer contains a threefold rotation axis whereas the *trans* isomer, **1**, has no symmetry. Therefore, in this isomer a given substituent on each chelate ring could in principle produce a separate resonance, but only a single resonance for the same substituent in each ring should occur in the *cis* form. This behavior has been observed in tris-(benzoylacetonato)[5] and tris(trifluoroacetylacetonato)[6] complexes of number of trivalent ions.



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We wish to report the preparation and isomeric identification of certain tris-chelate complexes of Co(III) which form only one isomer under ordinary conditions. The complexes studied are nitrogen-substituted derivatives of tris(salicylaldimine)cobalt(III) (**2**) and tris(pyrrole-2-aldimine)cobalt(III) (**3**).

(1) Alfred P. Sloan Foundation Fellow.

(2) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(3) V. Carassiti and M. Claudi, *Ann. Chim.* (Rome), **50**, 581 (1960); V. Carassiti and A. M. Marinangeli, *ibid.*, **50**, 593 (1960).

(4) H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960).

(5) R. C. Fay and T. S. Piper, *ibid.*, **84**, 2303 (1962).

(6) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).

(7) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).