

534. Preparation, Electronic Spectra, and Magnetic Properties of Some Transition-metal Isocyanato-complexes.

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The preparation of complexes of the type $(\text{Et}_4\text{N})_2\text{M}(\text{NCO})_4$, $\text{M} = \text{Mn}$, Co , Ni , Cu , and Zn , is described. *X*-Ray powder photographs show that the Mn^{II} , Ni^{II} , and Zn^{II} compounds are isomorphous with their Co^{II} analogue, and therefore contain tetrahedral tetrakisocyanatometallate(II) anions. The magnetic susceptibilities and the electronic spectra, including the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ transition for the nickel(II) compound, are reported and discussed. The copper(II) complex is not isomorphous with the others, but the results of spectral studies indicate that the arrangement of the donor nitrogen atoms in the $\text{Cu}(\text{NCO})_4^{2-}$ ion is probably that of a distorted tetrahedron.

THE pseudohalide ions can function as ligands in metal complexes. However, although there are numerous complex ions of the type MX_n^{m-} where $\text{X} = \text{CN}$, and a fair number where $\text{X} = \text{NCS}$, considerably less is known about those where $\text{X} = \text{NCO}$. Ripan¹ has reported the preparation of $\text{KCd}(\text{NCO})_3$, $\text{KCu}(\text{NCO})_3$, and also a group of compounds formulated as $[\text{M}^{\text{II}}\{(\text{CH}_2)_6\text{N}_4\}_2(\text{H}_2\text{O})_4][\text{M}'^{\text{II}}(\text{CNO})_4]$, where $\text{M}' = \text{Co}$, Ni , or Cu . The compound $\text{KCu}(\text{NCO})_3$ has also been described by Söderbäck.² However, the only transition-metal cyanato- or isocyanato-complex anion which has been well characterised is the tetrakisocyanatocobaltate(II) ion, which, although long known,³ has only recently been studied in detail.⁴ To provide more information concerning complexes with the NCO group we have isolated compounds containing the $\text{M}(\text{NCO})_4^{2-}$ ions, where $\text{M} = \text{Mn}$, Ni , Cu , or Zn , and report here the results of magnetic, spectral and *X*-ray diffraction studies on them.

The method found useful for the preparation of complex ions of this type is the exchange between the bromide ions of the MBr_4^{2-} species and cyanate ions from silver cyanate in acetone. This type of reaction is well known for the preparation of covalent isocyanates such as $\text{Si}(\text{NCO})_4$.⁵ The reactions take place quite rapidly and high yields of the desired complex anion are formed in solution, but some difficulty was encountered in the final purification of the solids. The complexes remain undecomposed in dry acetone or dry nitromethane for some hours, but they are quite labile in many other common

¹ Ripan, *Chem. Zentr.*, 1930, **12**, i, 967.

² Söderbäck, *Acta Chem. Scand.*, 1957, **11**, 1622.

³ Blomstrand, *J. prakt. Chem.*, 1871, [2], **3**, 221.

⁴ Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777.

⁵ See, e.g., Williams, "Cyanogen Compounds," Edward Arnold, 2nd edn., 1948.

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solvents, such as ethanol, unless an excess of tetraethylammonium cyanate is present. The nickel(II) and copper(II) complexes are hygroscopic, and samples of the former which had taken up water from the atmosphere could not be readily reconverted to the original blue material.

The molar electrolytic conductances of the complexes in nitrobenzene ($10^{-3}M$) at room-temperature are all in the range 50—60 $\text{ohm}^{-1} \text{cm}^2$, in agreement with their formulation as uni-bivalent electrolytes.

The results of magnetic and electronic spectral studies⁴ on potassium tetrakisocyanatocobaltate(II) and its analogue with the *n*-butyltriphenylphosphonium cation showed that the $\text{Co}(\text{NCO})_4^{2-}$ ion has an essentially tetrahedral arrangement of donor atoms around the cobalt(II) ion and that the NCO groups are, in fact, co-ordinated through the nitrogen atoms. Tetraethylammonium tetrakisocyanatocobaltate(II) has been used in the present work as a reference compound for isomorphism studies. The reflectance spectrum of this compound is quite analogous to those of the tetrakisocyanatocobaltate(II) complexes reported previously,⁴ and therefore the anion may reasonably be assumed to have a tetrahedral structure.

X-Ray powder photographs were obtained for all the compounds reported. The observed d values are given in Table I. Intercomparison of these photographs shows that the four compounds $(\text{Et}_4\text{N})_2\text{M}(\text{NCO})_4$, $M = \text{Mn, Co, Ni, and Zn}$, are isomorphous, but the powder photograph of the copper(II) complex differs from those of the other compounds. Thus the manganese(II), nickel(II), and zinc(II) complexes contain tetrahedral $\text{M}(\text{NCO})_4^{2-}$ ions.

TABLE I.
X-Ray powder data for the compounds $[\text{Et}_4\text{N}]_2[\text{M}(\text{NCO})_4]$.

$M = \text{Mn}$		Co		Ni		Cu		Zn	
d	Intensity	d	Intensity	d	Intensity	d	Intensity	d	Intensity
8.04	m	8.08	ms	8.08	ms	14.61	vw	8.04	ms
7.20	m	7.17	ms	7.14	ms	11.48	vw	7.14	ms
6.28	m	6.26	ms	6.26	m	8.55	w	6.24	m
5.61	m	5.56	m	5.57	ms	7.31	ms	5.57	m
5.05	s	5.05	s	5.04	s	6.33	m	5.05	s
4.72	ms	4.72	ms	4.72	ms	5.81	m*	4.72	m
4.09	s	4.06	s	4.07	s	5.47	mw	4.08	s
3.925	vw	3.92	vw	3.90	vw	4.695	vs	3.925	w
3.76	m	3.74	m	3.75	m	4.27	m	3.75	m
3.60	vw	3.58	w	3.58	vw	4.00	w	3.59	w
3.45	w	3.44	w	3.44	w	3.79	w	3.44	m
3.355	w	3.34	vw	3.35	w	3.64	mw*	3.35	w
3.20	w	3.17	vw	3.175	w	3.52	mw	3.175	w
3.10	w	3.10	w	3.10	w	3.37	w	3.10	w
2.99	vw	2.99	vw	2.97	vw	3.13	mw	2.98	vw
2.91	vw	2.885	vw	2.89	vw	2.98	vw	2.91	vw
						2.93	w		
						2.74	vw		
						2.61	vw		

* Broad line.

We shall now discuss the magnetic properties and the electronic spectra of the complexes in the light of the above structural information.

Manganese(II) Complex.—The magnetic moment of 5.98 B.M. at 296°K is in the range expected for a 6A_1 ground state. The electronic spectrum has been obtained for the solid and for acetonitrile solutions, and the results are shown in Table 2 and Fig. 1. In the solution spectrum there is a strong absorption edge in the ultraviolet region, probably due to a charge-transfer band lying above 40,000 cm^{-1} . The highest energy crystal field bands of the manganese(II) complex appear as shoulders on this absorption edge, so there is some uncertainty as to their exact energies. Moreover, molar extinction coefficients could not be obtained for these bands.

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Because of the observations mentioned above, comparison of the solid-state spectrum with that obtained for acetonitrile solutions may be made only for energies $< 29,000 \text{ cm}^{-1}$. In this region the spectra are virtually identical, indicating that the tetrahedral $\text{Mn}(\text{NCO})_4^{2-}$ ion is unaltered in acetonitrile. The spectrum resembles very closely the spectra reported previously^{6,7} for the tetrahalogenomanganate(II) ions. The molar extinction coefficients of the bands are similar in magnitude to those for MnCl_4^{2-} and MnBr_4^{2-} and are in accord with the suggested tetrahedral structure.

The group of three bands of lowest energy may be assigned as follows: ${}^6A_1 \longrightarrow {}^4T_1(G)$ at $\sim 20,400$, ${}^6A_1 \longrightarrow {}^4T_2(G)$ at $22,400$, ${}^6A_1 \longrightarrow {}^4E, {}^4A_1(G)$ at $23,300 \text{ cm}^{-1}$. The band at $36,700 \text{ cm}^{-1}$ and the shoulder at $\sim 35,800 \text{ cm}^{-1}$ on the side of the charge-transfer absorption edge may be reasonably assigned to the transitions ${}^6A_1 \longrightarrow {}^4T_2(F)$ and ${}^6A_1 \longrightarrow {}^4A_2$ and ${}^4T_1(F)$, respectively. The 4A_2 and 4T_1 levels from the 4F free ion term lie very close together for the values of Δ , the ligand field strength parameter, prevailing in tetrahedral manganese(II) complexes, and, in compounds of this type, the transitions to these levels are not usually resolved.^{6,7} However, the bands at $27,500$ and $\sim 26,000 \text{ cm}^{-1}$ cannot be unambiguously assigned, since three transitions, to ${}^4T_2(D)$, ${}^4E(D)$ and ${}^4T_1(P)$ upper states,

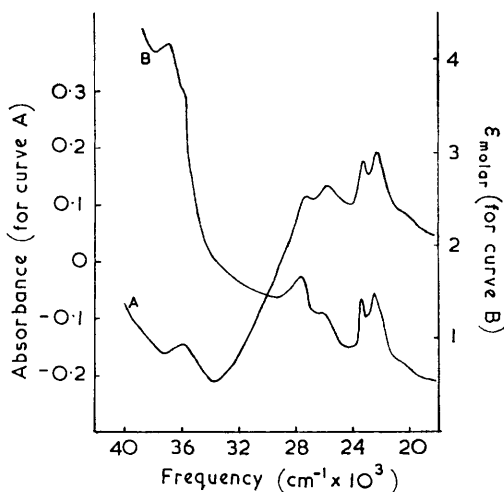


FIG. 1. Spectra of $[\text{Et}_4\text{N}]_2[\text{Mn}(\text{NCO})_4]$:
(A) solid by reflectance.
(B) 0.128M in $\text{CH}_3\cdot\text{CN}$.

are expected in this region. Moreover there is some uncertainty⁶⁻⁸ as to the amount by which the 4P free ion term should be reduced under the influence of ligand fields. Because the bands above $25,000 \text{ cm}^{-1}$ are either not clearly resolved or cannot be unambiguously assigned, we have not carried out a detailed quantitative analysis of the spectrum. However, some qualitative observations may be made.

First, the energies of the transitions to the levels ${}^4E, {}^4A_1(G)$ and ${}^4A_2(F)$, which are unaffected by the magnitude of Δ , but which depend upon the values of the effective interelectronic repulsion parameters B' and C' , are similar for both $\text{Mn}(\text{NCO})_4^{2-}$ and MnBr_4^{2-} . For MnBr_4^{2-} the bands were observed⁷ at $23,000 \text{ cm}^{-1}$ for ${}^6A_1 \longrightarrow {}^4E, {}^4A_1(G)$ and at $36,150 \text{ cm}^{-1}$ for ${}^6A_1 \longrightarrow {}^4A_2(F)$, compared with $23,300$ and $\sim 35,800 \text{ cm}^{-1}$ respectively for $\text{Mn}(\text{NCO})_4^{2-}$. This is in accord with the observation that the isocyanate group is in a similar position to the bromide ion in the nephelauxetic series.^{4,9}

Secondly, the close similarity between the term reductions for $\text{Mn}(\text{NCO})_4^{2-}$ and its bromo-analogue suggested that, even without a full calculation, use of the energy level diagram obtained⁷ for MnBr_4^{2-} would give at least a very approximate value of Δ from

⁶ Buffagni and Dunn, *Nature*, 1960, **188**, 937; Furlani and Furlani, *J. Inorg. Nuclear Chem.*, 1961, **19**, 51.

⁷ Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1962, **84**, 167.

⁸ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.

⁹ Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

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the splitting of the levels derived from 4G . From the energies of the ${}^4E, {}^4A_1(G) \rightarrow {}^4T_2(G)$ and ${}^4E, {}^4A_1(G) \rightarrow {}^4T_1(G)$ separations a Δ value of about 4600 cm.^{-1} was obtained. Although this value of Δ must be regarded as very approximate, it is in quite good agreement with (i) the value found for $\text{Ni}(\text{NCO})_4^{2-}$ (see Table 5), and (ii) the position of the isocyanate group in the spectrochemical series.⁹

Tetraethylammonium tetrakisocyanatomanganate(II) showed neither the yellowish-green fluorescence in ultraviolet radiation nor the similarly coloured triboluminescence, even on cooling to $\sim 80^\circ\text{K}$, that have sometimes been observed for other tetrahedral complexes of manganese(II).^{8,10}

The reflectance spectrum also contained a very weak band at $16,000 \text{ cm.}^{-1}$, due to trace quantities of $\text{Co}(\text{NCO})_4^{2-}$. The values for the respective molar extinction coefficients of the spectral bands of the manganese(II) and cobalt(II) species indicate that as little as 0.05–0.1 mole percent. of the cobalt(II) complex would give rise to this effect. Jørgensen also found traces of cobalt(II) in some samples of $(\text{Et}_4\text{N})_2\text{MnBr}_4$.⁸

Nickel(II) Complex.—The results of the magnetic and electronic spectral studies support the suggestion, made on the basis of the X-ray powder data, that the tetrakisocyanatonickelate(II) ion is essentially tetrahedral. The relatively high value of the magnetic moment at room temperature (3.70 B.M.) is in the range observed for nickel(II) in ligand fields with little departure from T_d symmetry.¹¹ Pronounced distortions of the ligand field, brought about by geometrical deviation from a rigorously tetrahedral arrangement, by the presence of two or more ligands with widely differing Δ values, or by both of these factors operating together, are usually apparent from the rather low magnetic moments which are obtained. For example, dichlorobis(triphenylphosphine)nickel(II), which is appreciably distorted both geometrically¹² and in terms of the differing ligand field strengths of the chloride ion and triphenylphosphine,¹³ has a magnetic moment of only 3.41 B.M. at room temperature.¹³

Figgis has calculated¹⁴ how the magnetic moment of nickel(II) in a field of T_d symmetry varies as a function of the spin-orbit coupling constant, λ , and temperature. The magnetic moment should, for reasonable values of λ , drop rapidly from the high values expected at room temperature to zero as the function $kT/|\lambda|$ approaches zero. The results of a study of the temperature dependence of the magnetic susceptibility of tetraethylammonium tetrakisocyanatonickelate(II) are shown in Table 3. Although the moment falls with

TABLE 2.

Electronic absorption spectra of $(\text{Et}_4\text{N})_2\text{M}(\text{NCO})_4$, M = Mn, Ni, Cu.

M	State	Absorption max.* (cm. ⁻¹ × 10 ³) (ϵ_{molar} for solns.)
Mn	Solid	27.2, 25.8, 23.1, 22.2, ~ 20.2 sh
	CH_3CN (0.128M)	36.7, †, ~ 35.8 sh, 27.5 (1.6), ~ 26.0 sh, 23.3 (1.3), 22.4 (1.4), ~ 20.4 sh
Ni	Solid	~ 18.4 sh, 16.6, 15.5, 12.8, 9.26, ~ 4.7
	CH_3NO_2 (0.036M)	~ 18.8 sh, 16.8 (142), 15.6 (142), 12.8 (5.8), 9.46 (24), ~ 4.6 (23)
Cu	Solid	25.2, §, 11.2
	CH_3NO_2 (0.0091M)	11.5 (58)

* Bands due to vibrational overtones have been omitted. † ϵ_{molar} not obtained as band is on the side of strong charge-transfer absorption. § Charge transfer band.

decreasing temperature, the values at temperatures approaching that of liquid nitrogen are not as small as would be predicted from the original calculations.¹⁴ Very similar

¹⁰ Goodgame and Cotton, *J.*, 1961, 3735, and refs. therein.

¹¹ Gill and Nyholm, *J.*, 1959, 3997; Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 5771, 5774; Donoghue and Drago, *Inorg. Chem.*, 1962, **1**, 866.

¹² Garton, Henn, Powell, and Venanzi, *J.*, 1963, 3625.

¹³ Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

¹⁴ Figgis, *Nature*, 1958, **182**, 1568.

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TABLE 3.

Magnetic data for $(Et_4N)_2M(NCO)_4$, M = Ni, Cu.

M = Ni			M = Cu		
T (°K)	$10^6 \chi_m$ (c.g.s.u.) *	μ_{eff} . B.M.†	T (°K)	$10^6 \chi_m$ (c.g.s.u.) *	μ_{eff} . B.M.†
324.6	5212	3.69	294.0	1653	1.98
303.5	5625	3.71	257.6	1917	1.99
296.0	5771	3.71	246.0	1974	1.98
283.2	5970	3.69	232.1	2094	1.98
273.5	6194	3.70	213.0	2214	1.95
254.0	6650	3.69	188.5	2453	1.93
203.0	8137	3.65	160.3	2812	1.91
188.0	8577	3.61	121.9	3696	1.91
174.4	9109	3.58			
151.0	10,350	3.55			
138.3	11,050	3.51			
115.7	12,820	3.46			
89.0	15,600	3.35			

* Corrected for diamagnetism. † Calc. from $\mu_{eff.} = 2.84(\chi_m T)^{\frac{1}{2}}$.

behaviour has been observed by Figgis,¹⁵ Lewis,¹⁶ and their co-workers for other tetrahedral nickel(II) complexes, and may be ascribed¹⁷ to electron delocalisation¹⁸ and small ligand field distortions.

The electronic spectrum of $(Et_4N)_2Ni(NCO)_4$ was obtained in the solid state and in nitromethane solution over the range 28,000—3800 cm^{-1} . The results are shown in Table 2 and Fig. 2. The spectra in the two phases are virtually identical, the major

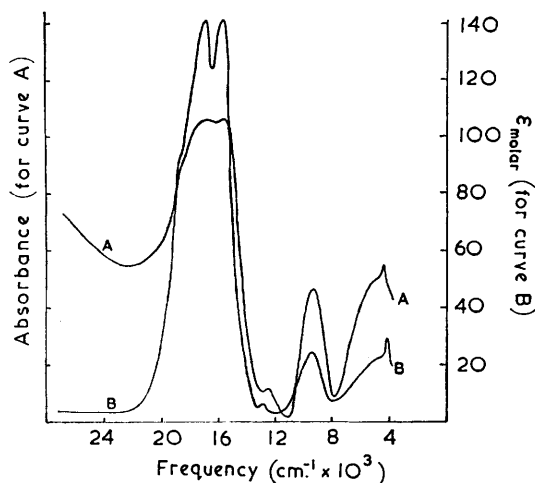


FIG. 2. Spectra of $[Et_4N]_2[Ni(NCO)_4]$:
(A) solid by reflectance.
(B) 0.036M in $CH_3 \cdot NO_2$.

differences in the solid-state spectrum being the rather poorer resolution of the band in the visible region and the apparent enhancement of the intensity of the weak bands. These effects are usually observed in reflectance spectra.

The bands may be assigned quite satisfactorily from Liehr and Ballhausen's energy level diagram¹⁹ for nickel(II) in T_d symmetry with $B = 810 \text{ cm}^{-1}$, $C = 3150 \text{ cm}^{-1}$, $\lambda = -275 \text{ cm}^{-1}$ and $\Delta = 4600 \text{ cm}^{-1}$ (see Table 4). The band due to ${}^3T_1(F) \rightarrow {}^3T_2(F)$ was not observed in its entirety owing to the limits of the range of the spectrophotometer, and there is some uncertainty as to the exact band maximum because of the presence of sharp

¹⁵ Figgis, Symposium on Ligand Field Theory, 140th Meeting of the American Chemical Society, Chicago, 1961.

¹⁶ Lewis, Symposium on Structure and Reactivity in Inorganic Chemistry, Chemical Society Annual Meeting, Sheffield, 1962.

¹⁷ Lewis, personal communication.

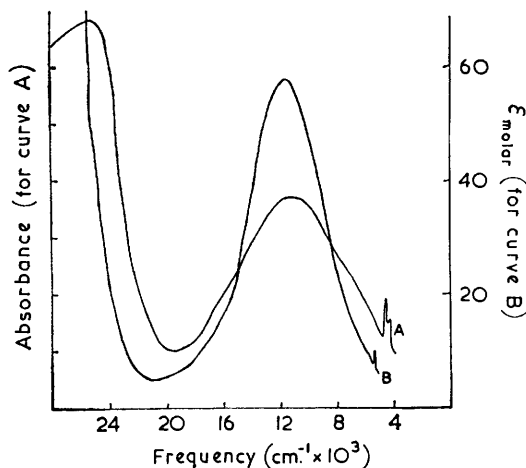
¹⁸ Stevens, *Proc. Roy. Soc.*, 1953, A, **219**, 542.

¹⁹ Liehr and Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

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bands at 4400 and 4180 cm^{-1} , due to vibrational overtones. These overtones were also present in the spectra of the other tetraisocyanatometallate(II) ions described here. Data concerning the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition for tetrahedral nickel(II) have been reported previously for various solid-state oxide or sulphide systems^{20,21} and for tetrahalogenonickelate(II) ions in halide melts, KBr wafers or in acetonitrile.²²

FIG. 3. Spectra of $[\text{Et}_4\text{N}]_2[\text{Cu}(\text{NCO})_4]$:
(A) solid by reflectance.
(B) 0.0091M in $\text{CH}_3\cdot\text{NO}_2$.



The shoulder at $\sim 18,800 \text{ cm}^{-1}$ is most probably due to the transition ${}^3T_1(F) \rightarrow {}^1T_2(G)$, which gains intensity by mixing with the spin-orbit component of ${}^3T_1(P)$ which has the same symmetry (Γ_5). Although the ${}^3T_1(P)$ level is a multiplet the theoretical energy spread for T_d symmetry is only about 700 cm^{-1} , and, in fact, the difference between the energies of the two main band maxima observed at 16,800 and

TABLE 4.

Observed band energies ($\text{cm}^{-1} \times 10^3$) for $(\text{Et}_4\text{N})_2\text{Ni}(\text{NCO})_4$ compared with values calculated from ref. 19, with $\Delta = 4600 \text{ cm}^{-1}$.

Designation of upper level	Calc.	Obs.*
${}^3T_2(F)$	4.8 †	~ 4.6
${}^3A_2(F)$	9.40	9.46
${}^1T_2(D)$	12.2	
${}^1E(D)$	12.8	12.8
${}^3T_1(P)$	16.35 †	15.6
		16.8
${}^1T_2(G)$	19.0	~ 18.8

* From solution spectrum. † Centre of multiplet.

$15,600 \text{ cm}^{-1}$ is in reasonable agreement with this. In order to spread out the ${}^3T_1(P)$ multiplet to cover the band at $18,800 \text{ cm}^{-1}$, considerable distortion would have to be invoked, which seems unlikely in view of the high value of the magnetic moment.

The intensities of the crystal-field bands of tetrahedral complexes have occasioned some theoretical interest,^{22,23} and Weakliem²¹ has discussed the matter in some detail for nickel(II) and cobalt(II) in the systems $\text{ZnS}, M^{\text{II}}$ and $\text{CdS}, M^{\text{II}}$. Since we have been unable to observe all of the band due to ${}^3T_1(F) \rightarrow {}^3T_2(F)$ for $\text{Ni}(\text{NCO})_4^{2-}$, we could not determine its oscillator strength. Owing to the ${}^3T_1(P) \rightarrow {}^1T_2(G)$ interaction, calculation of an accurate

²⁰ (a) Pappalardo and Dietz, *Phys. Rev.*, 1961, **123**, 1188; (b) Pappalardo, Wood, and Linares, *J. Chem. Phys.*, 1961, **35**, 1460.

²¹ Weakliem, *J. Chem. Phys.*, 1962, **36**, 2117.

²² (a) Boston and Smith, *J. Amer. Chem. Soc.*, 1963, **85**, 1006; (b) Ros, *Rec. Trav. chim.*, 1963, **82**, 823; (c) Hamer, *Mol. Phys.*, 1963, **6**, 257.

²³ Ballhausen and Liehr, *J. Mol. Spectroscopy*, 1958, **2**, 342; 1960, **4**, 190.

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oscillator strength for ${}^3T_1(F) \rightarrow {}^3T_1(P)$ from the area of the visible band is of little value. However, some indication of the relative intensities of the three spin-allowed bands may be obtained from the values of $\epsilon_{\max} \cdot \nu$ where ν is the half-band width. The relative intensities of these bands in increasing order of energy are 0.28 : 0.12 : 1.0. In calculating the value of $\epsilon_{\max} \cdot \nu$ for the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition an allowance was made for the asymmetry to higher energy. In agreement with the theoretical predictions, the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition is usually observed to be much stronger than the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ transition.^{20-22, 24} Weakliem's calculations for nickel(II) in zinc sulphide or cadmium sulphide matrices suggested that the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition should be somewhat weaker than ${}^3T_1(F) \rightarrow {}^3T_1(P)$, but the difference was not expected to be very great. However, the intensity observed by Weakliem for ${}^3T_1(F) \rightarrow {}^3T_2(F)$ was even smaller than that for ${}^3T_1(F) \rightarrow {}^3A_2(F)$. Although our measurements of the intensities of the bands of $\text{Ni}(\text{NCO})_4^{2-}$ must be taken as only an approximate indication of their relative magnitudes, it does appear that the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition more nearly approaches the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ transition in intensity than it does ${}^3T_1(F) \rightarrow {}^3T_1(P)$.

Copper(II) Complex.—Although the copper(II) complex is not isomorphous with its cobalt(II) or nickel(II) analogues, and therefore does not have a similar crystal structure, the X-ray results do not necessarily rule out a tetrahedral arrangement of ligands around the copper(II) ion. The results of a study²⁵ of the vibrational spectra of the compounds $(\text{Et}_4\text{N})_2\text{M}(\text{NCO})_4$, M = Mn, Co, Ni, Cu, and Zn, indicate that the NCO groups in the copper(II) complex are also bonded to the metal ion through the nitrogen atoms. We have examined the electronic spectrum of the complex in order to obtain more information concerning the structure of the $\text{Cu}(\text{NCO})_4^{2-}$ ion.

TABLE 5.

Comparison of values of Δ (cm^{-1}) for $\text{M}(\text{NCO})_4^{2-}$ (Δ_{NCO}) and MCl_4^{2-} (Δ_{Cl}), where M = Mn, Co, Ni.

	Δ_{NCO}	Δ_{Cl}^*	$\Delta_{\text{NCO}}/\Delta_{\text{Cl}}$
Mn	~4600 †	3600	~1.28
Co.....	4150 †	3200	1.30
Ni.....	4600	3600	1.28

* From ref. 7. † Approximate value, see text. ‡ From ref. 9.

The spectrum from 4000 cm^{-1} to the onset of strong charge-transfer absorption at ~24,000 cm^{-1} shows only one crystal-field band, apart from the sharp bands due to vibrational overtones in the 4000—6000 cm^{-1} region mentioned previously. The crystal-field band for nitromethane solutions appears to be quite symmetrical. In the solid state the band is at virtually the same energy as in solution, the difference being 300 cm^{-1} , but is somewhat broader.

If the $\text{Cu}(\text{NCO})_4^{2-}$ ion contains truly four-co-ordinate copper(II) the structure could be either planar or tetrahedral (possibly distorted). However, the copper(II) ion could achieve a higher co-ordination number by the presence of atoms at bonding distances axially to planar $\text{Cu}(\text{NCO})_4^{2-}$ groups by suitable crystal packing. This might be achieved by, for example, direct stacking of planar $\text{Cu}(\text{NCO})_4^{2-}$ ions to provide copper-copper interactions, or by placing cyanate oxygen atoms from one anion axially to another anion. Both of these cases would provide strongly tetragonal ligand fields.

The energy level scheme for tetragonally distorted octahedral copper(II), leading in the limit to a planar configuration, is well established theoretically and experimentally. The existence of a planar or a strongly tetragonal ligand field results in the presence of three bands, which may appear in the form of one very broad asymmetric band, due to

²⁴ Goodgame, Goodgame, and Cotton, *J. Amer. Chem. Soc.*, 1961, **83**, 4161; Furlani and Morpurgo, *Z. phys. Chem. (Frankfurt)*, 1961, **28**, 93.

²⁵ Forster and Goodgame, to be published.

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transitions from the ${}^2B_{1g}$ ground state to the excited states ${}^2B_{2g}$, 2E_g , and ${}^2A_{1g}$. Since we observe only one symmetrical band for $(Et_4N)_2Cu(NCO)_4$ in the range 4000—24,000 cm^{-1} , a planar or tetragonal ligand field for the copper(II) ion in this complex seems improbable. Moreover, the position of the band (11,500 cm^{-1}) is at considerably lower energy than the lowest energy crystal-field band observed²⁵ for $HgCu(NCS)_4$ (at 15,100 cm^{-1}) which is known²⁶ to have a structure such that the copper atom is surrounded by four nitrogen atoms at $1.90 \pm 0.04 \text{ \AA}$ and two sulphur atoms placed approximately in axial positions at $3.00 \pm 0.02 \text{ \AA}$, forming a distorted octahedron. Also the absence of any very pronounced antiferromagnetism for $(Et_4N)_2Cu(NCO)_4$ renders the existence of appreciable copper-copper interactions rather unlikely.

On the other hand, the spectral data are not inconsistent with the presence of a distorted tetrahedral ligand field. In T_d symmetry the 2D free ion term of copper(II) splits into a lower-lying 2T_2 level and a 2E upper level. Spin-orbit coupling splits the ground state further into two sub-levels Γ_7 and Γ_8 of the double group, while the upper state remains unsplit transforming as Γ_8 . For regular tetrahedral ligand fields we should expect one crystal field band at an energy equal to $\Delta + \zeta$, where ζ is the spin-orbit coupling constant which has a free ion value of 829 cm^{-1} for copper(II), and one at very low energy ($3\zeta/2$). The higher-energy band has been observed for the systems ZnO, Cu ^{21,27} and CdS, Cu ^{20b} for which the environments of the copper atoms are only slightly distorted from T_d symmetry. On this basis, the ligand field of $Cu(NCO)_4^{2-}$ does not appear to have T_d symmetry, since the band at 11,500 cm^{-1} would suggest a Δ value of $\sim 10,700 \text{ cm}^{-1}$ which seems unusually high compared with those found for the analogous compounds of cobalt(II) and nickel(II).

Ligand fields of lower symmetry provide pronounced splittings of the 2T_2 ground state and a much smaller splitting of the 2E excited state. Liehr²⁸ has provided the theoretical calculations for d^1 systems in low symmetry fields, and Piper and Karipides²⁹ have explained the existence of ligand-field bands at 8000 and 7570 cm^{-1} for $CuBr_4^{2-}$ on the basis of the distorted tetrahedral structure³⁰ of this ion. The tetrachlorocuprate(II) ion, which also has a distorted tetrahedral structure,³¹ has a rather broad ligand-field band at 8000—9000 cm^{-1} .³² On this basis, and since it appears that the Δ value of the isocyanate group is some 25—30% greater than that due to the chloride ion in tetrahedral cobalt(II) and nickel(II) complexes, the presence of a ligand field band at 11,500 cm^{-1} seems not unreasonable for $Cu(NCO)_4^{2-}$ with a distorted tetrahedral structure. Some additional support for this comes from the fact that the ligand-field band for solid solutions of copper(II) in $HgZn(NCS)_4$ is found at 10,500 cm^{-1} .²⁵

Figgis¹⁴ has calculated that the magnetic moments of regularly tetrahedral complexes of copper(II) should be ~ 2.2 B.M. at room temperature, and that there should be a departure from the Curie law. However, caesium tetrachlorocuprate(II) has a magnetic moment of only 2.00 B.M. at room temperature, and there is only a very small departure from the Curie law.³³ Tetraethylammonium tetrakisocyanatocuprate(II) has a similar moment at room temperature (1.98 B.M.) though, in this case, there is a departure from the Curie law at lower temperatures (see Table 3). However, as mentioned above, with ligand fields of lower symmetry the 2T_2 ground state is split and much of the orbital contribution to the magnetic moment will be destroyed. The magnetic measurements are therefore not inconsistent with the structure suggested above for $Cu(NCO)_4^{2-}$.

²⁶ Korczynski, *Roczniki Chem.*, 1962, **36**, 1539.

²⁷ Pappalardo, *J. Mol. Spectroscopy*, 1961, **8**, 554.

²⁸ Liehr, *J. Phys. Chem.*, 1960, **64**, 43.

²⁹ Karipides and Piper, *Inorg. Chem.*, 1962, **1**, 970.

³⁰ Morosin and Lingafelter, *Acta Cryst.*, 1960, **13**, 807.

³¹ Helmholtz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

³² Caglioti, Furlani, Cervone, and Valenti, 7th International Conference on Co-ordination Chemistry, Stockholm, 1962.

³³ Figgis and Harris, *J.*, 1959, 855.

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EXPERIMENTAL

Preparation of the Complexes.—The tetraethylammonium tetrakisocyanatometallate(II) compounds were all prepared by the following method. The appropriate tetraethylammonium tetrabromometallate(II) complex was shaken in acetone with a slight excess over the calculated quantity of silver cyanate. The mixture was filtered, and then diethyl ether added to the filtrate. The precipitated complexes were filtered off and purified. Further details for individual compounds are given below.

Tetraethylammonium tetrakisocyanatomanganate(II). This pale green *complex* was purified by dissolving it in acetone and reprecipitating with diethyl ether, followed by a similar treatment from nitromethane solution (45% yield, m. p. 218°) (Found: C, 49.5; H, 7.9; N, 17.6. $C_{20}H_{40}MnN_8O_4$ requires C, 49.7; H, 8.3; N, 17.4%); Λ_m in $PhNO_2 = 59.1 \text{ ohm}^{-1} \text{ cm}^2$.

Tetraethylammonium tetrakisocyanatocobaltate(II). Blue *complex*, recrystallised from ethanol (44% yield, m. p. 243°) (Found: C, 49.7; H, 8.5; N, 17.7. $C_{20}H_{40}CoN_8O_4$ requires C, 49.3; H, 8.3; N, 17.25%); Λ_m in $PhNO_2 = 55.0 \text{ ohm}^{-1} \text{ cm}^2$.

Tetraethylammonium tetrakisocyanatonickelate(II). This deep blue *complex* was obtained in 24% yield after two recrystallisations from acetone–diethyl ether, and was dried *in vacuo*. It is hygroscopic, m. p. 210° (Found: C, 49.2; H, 7.9; N, 16.7. $C_{20}H_{40}NiN_8O_4$ requires C, 49.3; H, 8.3; N, 17.25%); Λ_m in $PhNO_2 = 55.8 \text{ ohm}^{-1} \text{ cm}^2$.

Tetraethylammonium tetrakisocyanatocuprate(II). The green *complex*, recrystallised twice from acetone–diethyl ether, then twice from nitrobenzene–diethyl ether, was dried at 100° *in vacuo* for 6 hr. (40% yield, m. p. 118°) (Found: C, 43.9; H, 8.05; N, 17.5. $C_{20}H_{40}CuN_8O_4$ requires C, 48.8; H, 8.2; N, 17.1%); Λ_m in $PhNO_2 = 53.1 \text{ ohm}^{-1} \text{ cm}^2$.

Tetraethylammonium tetrakisocyanatozincate(II). Colourless *complex*, recrystallised from acetone–ethanol (30% yield, m. p. 243°) (Found: C, 48.1; H, 7.9; N, 16.7. $C_{20}H_{40}ZnN_8O_4$ requires C, 48.6; H, 8.2; N, 17.0%); Λ_m in $PhNO_2 = 54.0 \text{ ohm}^{-1} \text{ cm}^2$.

Physical Measurements.—Electrolytic conductances were measured on $10^{-3}M$ -solutions in nitrobenzene at 21°, using a Mullard E 7566 bridge and a conventional cell.

The reflectance spectra were obtained with a Beckman DK2 recording spectrophotometer, or with a Unicam S.P. 500 spectrophotometer. A Perkin-Elmer model 350 spectrophotometer was used for the solution spectra.

X-Ray powder photographs were taken with a Philips Debije–Scherrer powder camera, type PW 1024, 11.46 cm. diameter, using nickel-filtered copper radiation. The samples were enclosed in Lindemann tubes.

Magnetic measurements were made with a Gouy balance of essentially the same design as that described by Figgis and Nyholm.³⁴ The field was calibrated using an aqueous solution of AnalaR nickel chloride, the susceptibility of which is accurately known.³⁵ Using the value thus determined we obtained gram susceptibilities of 16.39×10^{-6} ($\pm 0.5\%$) at 293°K for $CoHg(SCN)_4$ and 10.86×10^{-6} ($\pm 0.5\%$) at 298°K for trisethylenediaminenickel(II) thiosulphate, in good agreement with the literature values of 16.44×10^{-6} and 10.82×10^{-6} , respectively, at these temperatures.^{36,37} Temperature was calibrated in the range 77–295°K with freshly recrystallised copper(II) sulphate pentahydrate, using a θ value of 0.7°³⁴ and checked with $CoHg(SCN)_4$, for which a θ value of 10° ($\pm 1^\circ$) was found, in agreement with that obtained by Figgis and Nyholm.³⁶ Temperature was calibrated in the range 295–445°K with $CoHg(SCN)_4$. Perspex Gouy tubes were used below room temperature and glass tubes above room temperature. Duplicate determinations were carried out for each compound. Values of μ_{eff} were calculated from the expression $\mu_{\text{eff}} = 2.84(\chi_A \cdot T)^{\frac{1}{2}}$, where χ_A is the molar susceptibility, corrected for the diamagnetic contributions using Pascal's constants, and T is the absolute temperature.

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³⁴ Figgis and Nyholm, *J.*, 1959, 331.

³⁵ Nettledon and Sugden, *Proc. Roy. Soc.*, 1939, A, 173, 313.

³⁶ Figgis and Nyholm, *J.*, 1958, 4190.

³⁷ Curtis, *J.*, 1961, 3147.