The Cyanoacetates of Manganese(II), Cobalt(II) and Zinc(II) and their Pyridine and 2,2'-Bipyridyl Complexes

M. CARTWRIGHT, D. A. EDWARDS and J. M. POTTS

School of Chemistry, University of Bath, Bath BA2 7AY, U.K.

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Anhydrous manganese(II), cobalt(II) and zinc(II) cyanoacetates have been prepared and characterized using spectroscopic, magnetic and X-ray powder photographic methods. The metal atoms in these octahedral polymeric compounds are surrounded by bridging and/or chelating carboxylate groups, together with N-bonded cyano-groups.

These cyanoacetates react with pyridine and 2,2'-bipyridyl to afford the octahedral complexes $M(O_2CCH_2CN)_2(py)_2$, (M = Mn, Co or Zn), and $Zn(O_2CCH_2CN)_2(bipy)$ which contain bidentate carboxylate groups, and $M(O_2CCH_2CN)_2(bipy)_2$, (M = Mn or Co), which contain unidentate carboxylate groups. Unlike the parent cyanoacetates, no metal–cyano-nitrogen interactions occur in these complexes.

Introduction

Metal acetates and halogenoacetates and their complexes have been investigated extensively. However substituted acetates in which the substituent contains a potential donor atom have not been studied to any significant extent. We have been exploring the chemistry of some metal cyanoacetates which, in view of the known Lewis basicity of the nitrogen of cyano-groups and the basicity of the cyano-group of cyanoacetic acid, may be expected to involve metal–nitrogen as well as the usual metal–carboxylate oxygen bonds. Very few simple cyanoacetates appear to have been reported and we know of no complexes derived from such carboxylates. Apart from the alkali metal cyanoacetates [1], information is available on the copper(I), copper(II) and cadmium(II) species.

Infrared spectroscopic evidence suggests that whereas the cyano-group is not co-ordinated to the metal in copper(I) cyanoacetate [2], both free and co-ordinated cyano-groups may be present in the polymeric copper(II) compound [3]. The magnetic properties of a probable hemi-hydrate, $[Cu(O_2CCH_2-CN)_2 \cdot 0.5H_2O]_n$, have also been reported [4]. A single-crystal X-ray diffraction study [5] of polymeric cadmium(II) cyanoacetate firmly establishes the presence of metal–cyano-nitrogen bonds. The octahedral environment around each cadmium atom comprises five carboxylate oxygen atoms and one cyano nitrogen atom. One cyanoacetate ligand is merely bidentate, the oxygen atoms bridging metal centres, whereas the other cyanoacetate ligand is terdentate with a bridging carboxylate moiety and a donor cyano-nitrogen atom bonding to a further cadmium atom in the infinite three-dimensional structure.

With potential cyano-co-ordination in mind, we therefore set out to prepare some further metal cyanoacetates, and report here the manganese(II), cobalt(II) and zinc(II) salts and their complexes with pyridine and 2,2'-bipyridyl.

Experimental

Preparation of Compounds

Manganese(II) and zinc(II) cyanoacetates

Hydrated manganese(II) chloride (10 g) or hydrated zinc(II) nitrate (10 g) was dissolved in the minimum volume of water and the metal carbonate precipitated by adding an excess of a saturated sodium carbonate solution. The freshly precipitated carbonate was filtered off, washed with water and then suspended in water (250 cm³) and solid cyanoacetic acid added with stirring until the solution reached pH 3 and all effervescence had ceased. The solution was then evaporated to dryness whilst small quantities of cyanoacetic acid were added. The products (Mn, very pale pink; Zn, colourless) were washed several times with anhydrous acetone and then dried and stored *in vacuo*.

On occasions the above method, or a similar one using hydrated manganese(II) nitrate as starting material, afforded the manganese salt as a dihydrate. This product was easily dehydrated by heating *in vacuo* at 120 °C for a few hours.

Cobalt(II) cyanoacetate

Cobalt(II) carbonate (20 g) was suspended in water and cyanoacetic acid added with stirring until all effervescence had ceased. Evaporation of the solu-

TABLE I. Analyses, Conductivities and Magnetic Moments.

Compound	% Yield	% Metal		% C		% H		% N		Λ_M S cm² mol⁻¹ 25 °C, 10⁻³ M MeCN	μ(B.M.) 297 K
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
Mn(O₂CCH₂CN)₂	50	24.7	24.6	32.4	32.3	1.77	1.81	12.5	12.6	Insoluble	5.63
Mn(O₂CCH₂CN)₂·2H₂O	45	20.9	21.2	28.5	27.8	2.82	3.12	11.7	10.8		4.67
Co(O₂CCH₂CN)₂	97	25.5	25.9	31.7	31.7	1.85	1.78	12.6	12.3	Insoluble	Diamagnetic
Zn(O₂CCH₂CN)₂	54	28.1	28.0	29.9	30.8	1.87	1.73	11.8	12.0	Insoluble	5.87
Mn(O₂CCH₂CN)₂(py)₂	87	14.6	14.4	48.0	50.4	3.62	3.71	13.2	14.7	15.1	5.26
Co(O₂CCH₂CN)₂(py)₂	63	15.6	15.3	49.3	49.9	3.55	3.67	13.9	14.5	10.2	Diamagnetic
Zn(O₂CCH₂CN)₂(py)₂	78	16.7	16.7	49.3	49.1	3.83	3.61	14.6	14.3	10.7	5.99
Mn(O₂CCH₂CN)₂(bipy)₂	90	10.3	10.3	57.5	58.3	3.80	3.78	15.5	15.7	23.0	Diamagnetic
Co(O₂CCH₂CN)₂(bipy)₂	73	10.9	10.9	57.4	57.9	3.70	3.71	15.1	15.6	24.3	
Zn(O₂CCH₂CN)₂(bipy)	84	17.0	16.8	48.9	49.3	3.04	3.11	14.2	14.4	12.5	Diamagnetic

tion to dryness, whilst adding small quantities of cyanoacetic acid gave a bright pink-coloured mass which was washed well with anhydrous acetone before drying and storage in vacuo.

Bis(pyridine)cobalt(II) cyanoacetate

Co(O₂CCH₂CN)₂ (3.0 g) and redistilled pyridine (2.1 cm³) were added to 2,2-dimethoxypropane (30 cm³) and the reactants kept at room temperature under nitrogen for 2 days. A pale pink product slowly formed, so a further 0.5 cm³ of pyridine was added and the reaction allowed to proceed for a further 3 days. The product was then filtered off, washed with ethanol and dried and stored in vacuo.

Bis(pyridine)manganese(II) cyanoacetate

Mn(O₂CCH₂CN)₂ (3.0 g) and redistilled pyridine (4.0 cm³) were allowed to react in 2,2-dimethoxypropane (35 cm³) at ca. 40 °C under nitrogen for 4 days. The almost colourless product was then filtered off, washed with 2,2-dimethoxypropane, then diethyl ether before drying and storage in vacuo.

Bis(pyridine)zinc(II) cyanoacetate

Zn(O₂CCH₂CN)₂ (3.0 g) was treated with pyridine (15 cm³) at room temperature under nitrogen for 3 days. A large excess of diethyl ether was then added to precipitate the product which was filtered off, washed with diethyl ether and dried and stored in vacuo.

Bis(2,2'-bipyridyl)cobalt(II) cyanoacetate

Co(O₂CCH₂CN)₂ (3.0 g) and 2,2'-bipyridyl (4.5 g) were added to 2,2-dimethoxypropane (30 cm³) under nitrogen. As the reaction appeared to be extremely slow at room temperature, the reaction mixture was kept at ca. 60 °C for 2 days. The apricot-coloured product was then filtered off, washed with 2,2-dimethoxypropane and dried in vacuo.

Bis(2,2'-bipyridyl)manganese(II) cyanoacetate

This cream-yellow-coloured complex was prepared in a similar manner to the cobalt analogue, except that the reaction was allowed to proceed for 4 days at room temperature.

(2,2'-Bipyridyl)zinc(II) cyanoacetate

Zn(O₂CCH₂CN)₂ (2.0 g) and 2,2'-bipyridyl (2.8 g) were allowed to react in anhydrous chloroform (50 cm³) for 2 days at room temperature. After filtration and washing with chloroform, the product was dried in vacuo. Yields and analyses are given in Table I.

TABLE II. Variable Temperature Magnetic Results.

T (K)	$Mn(O_2CCH_2CN)_2$		$Co(O_2CCH_2CN)_2$	
	$10^6 \, \chi_M^{corr}$ emu/mol	μ (B.M.)	$10^6 \, \chi_M^{corr}$ emu/mol	μ (B.M.)
333	11982	5.67	8261	4.71
313	12712	5.66	8776	4.71
297	13252	5.63	9127	4.67
273	14642	5.68	9930	4.68
253	15902	5.70	10770	4.70
233	16882	5.63	11512	4.65
213	18522	5.64	12582	4.65
193	20252	5.61	13722	4.62
173	22472	5.60	15262	4.61
153	25022	5.56	17142	4.60
133	28812	5.56	19612	4.59
113	33112	5.49	22482	4.53

Physical Measurements

Nujol and hexachlorobutadiene mull infrared spectra were recorded using a Perkin-Elmer 597 spectrophotometer. Mid- and far-infrared spectra of vaseline mulls or samples pressed in polythene were measured on a Grubb-Parsons DM4 spectrophotometer and a Beckman-R.I.I.C. FS720 interferometer. Raman spectra of solid samples were recorded using a Spex 1401 spectrometer in conjunction with a Spectra-Physics 125 He–Ne laser. Electronic spectra were obtained on a Unicam SP 700C spectrophotometer fitted with the standard diffuse reflectance attachment.

Magnetic susceptibility measurements between 113 and 333 K were obtained using a Newport Instruments variable temperature Gouy balance system, with $[Ni(en)_3]S_2O_3$ and $HgCo(NCS)_4$ as calibrants. Conductivities were measured at 25 °C using a Wayne Kerr autobalance bridge and dip-type cell with platinum electrodes. Thermogravimetric studies were carried out on a Stanton TR 1 automatic direct-reading balance. Samples were heated to 1000 °C using a heating rate of 4 °C per minute.

X-ray powder photographs of samples held in 0.5 mm diam. Lindemann glass tubes were taken on a 114.83 mm Philips Debye-Scherrer camera with nickel-filtered $CuK\alpha$ radiation ($\lambda = 1.5418$ Å).

A computer program developed by Taupin [6] and locally modified, was used to determine lattice type, unit cell dimensions and indices of the reflections. The approach adopted in the program is based on combination theory. Indices h k and l are assigned to the first lines (equivalent in number to the number of unknown parameters) which satisfy the equations of the type

$$h_i^2 A + k_i^2 B + l_i^2 C + 2h_i k_i D + 2k_i l_i E + 2l_i h_i F = Q_i$$

where $Q_i = 1/d_i^2$, $A = a^{*2}$, $B = b^{*2}$, $C = c^{*2}$, $D = a^*b^*$, $E = b^*c^*$, $F = c^*a^*$ and i = 1 to n. a^*, b^* and c^* are

the usual vectors defining the reciprocal lattice unit cell. The program systematically varies $h_i k_i l_i$ to find solutions which index all lines. The number of trials made is reduced by applying conditions such as symmetry, *i.e.* A=B=C and D=E=F = 0 for a cubic system, and A ⩾ B ⩾ C which prevents equivalent cells related by permutation and translation being considered.

For use with this program the input data of the line position has to be measured to an accuracy of better than 0.03° in 2θ, particularly for the lower symmetry classes, to prevent a large number of ill fitting cells being found.

Carbon, hydrogen and nitrogen were determined by microanalyses. Cobalt was determined as the anthranilate or as $Co(py)_4(NCS)_2$, manganese as the ammonium phosphate and zinc as the anthranilate.

Results and Discussion

The Cyanoacetates

The anhydrous cyanoacetates of manganese(II), cobalt(II) and zinc(II) have been obtained by reaction of the carboxylic acid with freshly prepared metal(II) carbonate. On occasions the manganese-(II) carboxylate was isolated as a dihydrate, but this could easily be dehydrated by heating *in vacuo* at 120 °C.

Anhydrous cobalt(II) acetate is known [7] to be an octahedral polymer, the complicated structure including four types of bridging acetate groups, one of which is also chelating. Three inequivalent cobalt-(II) sites are present, two of which have the metal atoms co-ordinated to six different acetate groups, whilst the third has an environment of four different types of bridging acetates and one chelating acetate. As will be shown below, the manganese(II) and

TABLE III. Diffuse Reflectance Electronic Spectra (cm^{-1})

Compound	Peak Maxima	Assignment
$Mn(O_2CCH_2CN)_2$	17900 vw	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
	22100 vw	$\rightarrow {}^4T_{2g}(G)$
	24300 vw, sp	$\rightarrow {}^4E_g(G), {}^4A_{1g}(G)$
	28500 vw	$\rightarrow {}^4T_{2g}(D)$
	45400 br	Charge transfer
$Co(O_2CCH_2CN)_2$	7700	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
	18600 ⎫	
	20400 sh ⎬	$\rightarrow {}^4T_{1g}(P)$
	21500 sh ⎭	
	40250	Charge transfer
	48400	Charge transfer
$Zn(O_2CCH_2CN)_2$	34000	Charge transfer
$Co(O_2CCH_2CN)_2(py)_2$	8200	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
	19800 ⎫	$\rightarrow {}^4T_{1g}(P)$
	20600 sh ⎬	
	38900 v, br	Charge transfer
	43400	Charge transfer
$Co(O_2CCH_2CN)_2(bipy)_2$	8000 ⎫	
	10000 ⎬	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
	11700 ⎭	
	13200 vw	$\rightarrow {}^2E_g$
	20400	$\rightarrow {}^4T_{1g}(P)$
	20700 br	Charge transfer
	30000 br	Charge transfer
	32900 br	Charge transfer
	42400 br	Charge transfer

[a]w, weak; sh, shoulder; sp, sharp; br, broad.

cobalt(II) cyanoacetates are also octahedral polymers and it is likely that the zinc(II) salt is similar. Thus in these compounds the cyanoacetate ligands must behave in a multidentate fashion, the two oxygen atoms of each ligand bridging and/or chelating metal atoms. This bonding may also be supported by metal–cyano nitrogen linkages, as has been found in a structural study [5] of cadmium(II) cyanoacetate. The lack of solubility of the anhydrous cyanoacetates in polar organic solvents such as acetonitrile and dimethylformamide also suggests that these compounds are polymeric in the solid state.

Magnetic measurements on the manganese(II) and cobalt(II) cyanoacetates over the temperature range 333–113 K, (Table II), show the magnetic moments to be within the ranges associated with high-spin octahedral environments for these metal ions [8]. Reciprocal molar susceptibility-temperature plots indicate Curie–Weiss magnetic behaviour over the temperature range employed, with θ values of 8 and 14 K for the manganese(II) and cobalt(II) salts respectively. These very small Weiss constants imply the absence of any significant antiferromagnetic coupling which could be conceivable via carboxylate bridges. Anhydrous cobalt(II) acetate also displays [9] Curie–Weiss magnetic behaviour over the range 66–300 K with μ_{eff} of 4.82 B.M. and θ of 4.8 K. The compounds are slightly less paramagnetic than most high-spin octahedral cobalt(II) and manganese-(II) compounds, and for cobalt(II) cyanoacetate this may be indicative of distortion which would split the $^4T_{1g}$ ground term, the orbital contribution thereby being partially quenched [10]. Such a distortion could result from a co-ordinated cyano-group, the cobalt(II) ions thereby possessing, for example, O_5N environments. Manganese(II) acetate is known [11]

TABLE IV. Selected Infrared Bands of the Cyanoacetates (cm^{-1}).

Na	Mn	Mn·$2H_2O$	Co	Zn	Assignment
2254 m	2275 s	2270 ms	2275 s	2275 s	ν(CN)
2258[a]	2276[a]	2278[a]	2280[a]	2255 sh	
1596 vs	1635 sh	1630 sh	1650 sh	1666 vs, br	$\nu(CO_2)_{asym}$
	1603 vs, br	1600 vs, br	1600 vs, br	1650 sh	
	1560 sh		1540 sh		
1422 ms	1421 s	1430 m	1423 s	1420 s	$\nu(CO_2)_{sym}$
1405 ms	1395 s	1390 s	1395 s	1402 s	
715 m	720 s	718 s	728 s	720 s	CO_2 scissors
506 m	512 ms	508 ms	515 ms	541 m	CO_2 wag
394 mw	430 ms	425 ms	439 ms	424 mw	C–C≡N bend
				396 w	
371 vw	378 m	374 m	387 m	364 m	CO_2 rock
191	208	210	205	264	$\Delta = \nu(CO_2)_{asym} - \nu(CO_2)_{sym}$
171	182	170	177	246	

[a]Raman data.

to display a similarly rather low μ_{eff} of 5.68 B.M. Zinc(II) cyanoacetate, as expected, is diamagnetic.

The electronic spectra of manganese(II) and cobalt(II) cyanoacetates are also quite consistent with octahedral microsymmetry [12]. The manganese(II) salt is faintly pink, as expected for a high-spin octahedral compound, and although the diffuse reflectance spectrum is rather poorly defined, sensible assignments, (Table III), of the spin-forbidden transitions can be made. The spectrum of the cobalt(II) salt shows only two of the three spin-allowed octahedral crystal field transitions, the 'two-electron' $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition not being observed. The main visible region band, essentially $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, is split into a number of components, as often found for high-spin octahedral cobalt(II) compounds. The interpretation of such band structure has been discussed [13], but if in the present case a CoO_5N chromophore is present the degeneracy of the $^4T_{1g}(P)$ level will necessarily be lifted, and splitting will be expected. Assuming octahedral co-ordination, approximate 10Dq, B and β values of 8780 cm^{-1}, 798 cm^{-1} and 0.82 respectively were obtained using the graphical method of Lever [12]. As would be anticipated, these values are quite similar to those of anhydrous cobalt(II) acetate [14, 15], although the cyanoacetate has a marginally smaller 10Dq value. The β value suggests only a minimal amount of electron delocalisation between metal and the ligands.

The infrared spectra of the cyanoacetates have been measured between 4000 and 100 cm^{-1}. Since detailed structures are unknown, the assignments (Table IV) are based on those previously made [1] for sodium cyanoacetate and cyanoacetic acid. Comments will mainly be restricted to the ν(CN), δ(CCN), $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ modes, as these are of particular significance in suggesting reasonable structures. The spectrum of sodium cyanoacetate which can

be taken as illustrative of an ionic situation with no metal–cyano nitrogen bonding, shows ν(CN) at 2254 cm^{-1}. Cadmium(II) cyanoacetate [5], however, has ν(CN) bands at 2291 and 2263 cm^{-1}, assignable to co-ordinated and unco-ordinated cyano-groups respectively. Such an increase in ν(CN) on co-ordination to a metal by σ-donation from nitrogen has been well established for organonitrile–metal complexes [16]. The metal(II) cyanoacetates studied in the present work all have ν(CN) frequencies some 20 cm^{-1} higher than that of the sodium salt so we believe that the cyanoacetate ligands are bonded to the metals by M ← N≡C– linkages as well as by the usual metal–oxygen bonds. The spectrum of the zinc salt alone also shows a pronounced shoulder at 2255 cm^{-1}, so like cadmium(II) cyanoacetate, the zinc analogue may possess both co-ordinated and unco-ordinated cyano-groups. These infrared results have been confirmed by measuring Raman spectra of the compounds in the ν(CN) region, as shown in Table IV. Further evidence of cyano-nitrogen co-ordination comes from a consideration of the frequencies of the δ(CCN) bending modes. It is known [16] for nitrile complexes that M ← N≡CR co-ordination brings about a frequency increase for this mode. Similarly, the frequency of this vibration for the cyanoacetates is some 40 cm^{-1} higher than for the analogous band of the sodium salt. Since two δ(CCN) bands are observed for the zinc salt, at 424 and 396 cm^{-1}, we believe these are associated with co-ordinated and unco-ordinated cyano-groups respectively. These ν(CN) and δ(CCN) frequency increases are not as large as those found for organonitrile complexes, but this is to be expected as carboxyl-oxygen co-ordination is also present which will remove electron density from the carboxyl group and hence tend to lower the ν(CN) and δ(CCN) frequencies.

TABLE V. Low Frequency Infrared Spectra (cm^{-1}).

$Mn(O_2CCH_3)_2$	$Mn(O_2CCH_2CN)_2$	$Co(O_2CCH_3)_2$	$Co(O_2CCH_2CN)_2$	$Zn(O_2CCH_3)_2$	$Zn(O_2CCH_2CN)_2$
330 m	290 s	322 s	303 s	278 s, v, br	310 m
273 s, br	286 sh	239 s	286 m	188 m, br	269 m
188 s, br	265 m	205 m	224 s	107 w	234 s, br
168 m	210 s	193 m	215 sh		215 s
115 w	147 s	161 m	196 s		181 s
	129 w		183 m		154 m
	115 s		151 s		125 m
			132 s		110 w

The positions of $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ bands of metal carboxylates and their separation, Δ, have been used many times [13, 17, 18] in attempts to determine the probable co-ordination modes of carboxylate groups. Thus, unidentate co-ordination will shift $\nu(CO_2)_{asym}$ to higher and $\nu(CO_2)_{sym}$ to lower frequencies compared to the free carboxylate ion situation, resulting in a greater Δ value. These shifts are related to a loss of equivalence of the C–O bonds of the free ion on co-ordination. There is no such basis for expecting a clear distinction in spectra between ionic, chelating and bridging carboxylates, the Δ values being quite similar. The cyanoacetates all exhibit one major $\nu(CO_2)_{asym}$ band together with one or more shoulders, whereas two $\nu(CO_2)_{sym}$ bands are evident for each compound. Two Δ values are therefore given in Table 4 for each compound, obtained by taking frequency differences between the major $\nu(CO_2)_{asym}$ band and each $\nu(CO_2)_{sym}$ band. Since the Δ values of the manganese(II) and cobalt(II) salts are very similar to those of the sodium salt it is clear that the cyanoacetate groups are not unidentate and are thus multidentate by chelating and/or bridging oxygen bonding as well as by cyano-nitrogen bonding. However, $\nu(CO_2)_{asym}$ is found some 60 cm^{-1} higher for zinc cyanoacetate whereas the $\nu(CO_2)_{sym}$ bands are found at similar frequencies to those of the other cyanoacetates. The Δ values for this compound are therefore tending towards a unidentate oxygen-bonded situation, although no example of unidentate cyanoacetate has been established. We incline to the view that the structure of zinc(II) cyanoacetate may differ from those of manganese(II) and cobalt(II) cyanoacetates, in that not only are both co-ordinated and unco-ordinated cyano-groups present as discussed above, but also in that the carboxylate oxygen bonding may be unsymmetrical even though still chelating or bridging. The frequency of the CO_2 wag of the zinc compound is also found some 30 cm^{-1} higher than those of the other cyanoacetates.

Although the infrared spectra of metal carboxylates have been extensively studied in the rock salt region, relatively little information is available for the lower frequency region where metal–oxygen stretching modes would be expected. Recently the metal isotope shift method has been used to advantage in assigning $\nu(CuO)$ of copper(II) carboxylate complexes [19] and these results together with a few other studies [20] place such modes below 400 cm^{-1}. Apart from the CO_2 rocking mode at 371 cm^{-1}, sodium cyanoacetate shows only a shoulder at 244 cm^{-1} assigned [1] to the in-plane C–CN bend and three weak bands between 200 and 100 cm^{-1} due to lattice or torsion modes. The cyanoacetates studied in this work, however, have rich low-frequency infrared spectra (Table V). Although definitive assignments are not possible because of the complexity and uncertainty of the structures involved, these bands are clearly associated with metal–oxygen modes, as we have observed similar bands in the spectra of the analogous acetates, which are also polymeric octahedral compounds [7] with bridging and chelating carboxylate ligands. Copper(II) cyanoacetate also shows several bands in this region ascribed [3] to metal–oxygen modes.

The thermal decomposition of each cyanoacetate was studied in a thermogravimetric analysis apparatus, the heating being carried out in air. Manganese(II) cyanoacetate dihydrate loses its water of crystallisation by 120 °C, the anhydrous compound then decomposing between 230 and 420 °C to give MnO which is further oxidised to Mn_2O_3 by 570 °C and subsequently to Mn_3O_4 by 950 °C. Cobalt(II) cyanoacetate decomposes between 190 and 440 °C to afford Co_2O_3 which is oxidised to Co_3O_4 between 950 and 980 °C. Zinc(II) cyanoacetate merely decomposes between 180 and 570 °C to give ZnO. The identities of the oxides were established by metal analyses and by X-ray powder photography. The observed t.g.a. weight losses were normally within 1% of the theoretical weight losses.

Since cadmium(II) cyanoacetate [5] is known to be monoclinic ($a = 4.465$, $b = 10.262$, $c = 17.567$ Å, $\beta = 95.44°$, $U = 801.3$ Å^3) it was felt worthwhile to examine the X-ray powder patterns of the anhydrous cyanoacetates reported here to establish whether or not these compounds crystallise in the same crystal

TABLE VI. X-Ray Powder Data for the Cyanoacetates.[a]

$Mn(O_2CCH_2CN)_2$			$Co(O_2CCH_2CN)_2$			$Zn(O_2CCH_2CN)_2$		
d_{expt}	d_{calc}	h k l	d_{expt}	d_{calc}	h k l	d_{expt}	d_{calc}	h k l
9.80	9.80	0 0 1	6.70	6.75	1 $\bar{2}$ 0	7.30	7.34	0 0 1
8.90	8.95	1 $\bar{1}$ 0	6.36	6.37	0 0 1	5.73	5.73	1 1 0
6.80	6.82	1 $\bar{2}$ 0	6.10	6.08	2 0 0	5.18	5.20	1 $\bar{2}$ 0
5.60	5.60	1 $\bar{2}$ 1	5.80	5.78	1 2 0	3.84	3.84	1 $\bar{3}$ 1
4.64	4.65	1 3 0	5.43	5.41	1 $\bar{1}$ 1	3.77	3.77	1 3 1
4.55	4.57	1 $\bar{3}$ 1	4.23	4.23	1 3 0	3.67	3.67	0 0 2
4.48	4.47	2 $\bar{2}$ 0	3.99	3.99	2 $\bar{2}$ 1	3.44	3.44	0 2 2
4.34	4.35	2 $\bar{1}$ 1	3.56	3.56	2 2 1	3.35	3.34	1 $\bar{5}$ 0
4.06	4.06	1 $\bar{4}$ 0	3.48	3.47	2 $\bar{3}$ 1	3.30	3.30	0 6 0
3.95	3.94	2 $\bar{3}$ 0	3.31	3.31	1 4 0	3.09	3.09	1 1 2

$a = 17.041$ A	$a = 14.668$ A	$a = 19.790$ A
$b = 9.850$ A	$b = 12.353$ A	$b = 6.030$ A
$c = 9.802$ A	$c = 6.372$ A	$c = 7.338$ A
$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
$\beta = 96.95°$	$\beta = 100.03°$	$\beta = 91.29°$
$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
$U = 1633.3$ A^3	$U = 1136.9$ A^3	$U = 875.4$ A^3

[a]The first 30 lines of each compound have been indexed. Only the first 10 are listed here.

class and are isomorphous with the cadmium salt. As we have shown by vibrational spectroscopy that zinc(II) cyanoacetate appears to contain both co-ordinated and unco-ordinated cyano-groups, as does the cadmium salt, and both metals are in the same sub-group of the Periodic Table, we were particularly interested to find out if these two compounds are closely related structurally. The large number of lines apparent in the powder photographs of all three cyanoacetates ruled out a crystal class of high symmetry, so indexing of the lines and determination of unit cell dimensions was most conveniently achieved using a computer program, the principles [6] of which have been outlined in the Experimental section. Using an upper limitation on unit cell volume of 2000 Å^3 and taking the first 30 lines of each photograph, successful indexing was achieved for each compound. The unit cell dimensions are given in Table VI, together with, by way of illustration, the experimental and calculated d spacings of the first 10 lines of each compound. Although each compound is monoclinic, with a primitive lattice, like the cadmium salt, the unit cell dimensions vary considerably from one compound to another and the cyanoacetates are therefore unlikely to be closely related structurally, either with each other or with the cadmium salt. The large unit cell volumes imply that Z must be high, as has been established [21] for anhydrous manganese(II) acetate (tetragonal, Z = 12) and cobalt acetate (orthorhombic, Z = 20).

Complexes with Pyridine and 2,2'-Bipyridyl

Manganese(II), cobalt(II) and zinc(II) cyano-acetates each react with pyridine to give $M(O_2CCH_2-CN)_2(py)_2$ whereas with 2,2'-bipyridyl the products are $M(O_2CCH_2CN)_2(bipy)_2$ (M = Mn or Co) and $Zn-(O_2CCH_2CN)_2(bipy)$. The preparations have normally been carried out in 2,2-dimethoxypropane, a solvent previously [22] employed to ensure anhydrous conditions. This reagent reacts with adventitious water giving acetone and methanol, neither of which will compete effectively with the heterocyclic nitrogen donor ligands for a co-ordination site around the metal. Conductivity measurements in acetonitrile (Table I), show the complexes to be essentially non-conductors in this solvent, implying that both cyano-acetate groups are co-ordinated to the metal in each complex. A uni–univalent electrolyte at a concentration of 10^{-3} M in acetonitrile would be expected [23] to have a molar conductance of 100–140 S cm^2 mol^{-1}.

The room temperature magnetic moments of the manganese(II) and cobalt(II) complexes (Table I) are indicative [8] of octahedral environments for the high-spin metal ions, the zinc complexes being, as expected, diamagnetic. The electronic spectra of the cobalt(II) complexes are also consistent with octahedral microsymmetry. As for the cyanoacetate itself, only ν_1 and ν_3 of the three spin-allowed crystal field transitions are observed, although a very weak band centred at 13,200 cm^{-1} for $Co(O_2CCH_2CN)_2(bipy)_2$

TABLE VII. Selected Infrared Bands for the Complexes (cm^{-1}); (X = O_2CCH_2CN).

$MnX_2(py)_2$	$CoX_2(py)_2$	$ZnX_2(py)_2$	$MnX_2(bipy)_2$	$CoX_2(bipy)_2$	$ZnX_2(bipy)$	Assignment
2245 ms	2250 m	2248 m	2250 m	2250 m	2248 m	ν(CN)
2250[a]	2248[a]	2247[a]	2251[a]		2246[a]	
1662 s	1645 vs, br	1655 vs	1635 sh	1640 s, br	1640 sh	$\nu(CO_2)_{asym}$
1620 sh	1615 s	1617 sh	1625 vs	1605 m	1622 vs	
1410 s	1408 sh	1410 m	1402 m	1395 m	1408 m	$\nu(CO_2)_{sym}$
1398 ms	1380 s	1385 s	1385 sh		1400 sh	
387 vw	387 vw	392 vw	378 vw	391 w	392 vw	–C–C≡N bend
357 w	363 w	358 w	360 w	381 w	366 w	CO_2 rock
285 m	298 s	292 m	~290 br, sh	298 m	285 sh	ν(MO) + ν(MN)
270 ms	268 s	267 s	~270 sh	264 s	275 m	
235 s	232 s	253 sh	237 s	232 s	255 m	
225 sh	212 sh	229 s	220 s	220 sh	243 m	
195 s	198 s	208 m	180 m	198 s	199 ms	
186 sh		195 s		183 w	181 s	
		183 s				
156 m	154 m	173 s	159 m	151 m	164 m	Unassigned
110 w	137 w	139 m	137 w	137 m	146 mw	
			110 w	117 w	142 mw	
				103 w	107 w	
419 m	427 ms	424 m	430 w	417 s	435 vw	Ligand bands
			411 ms	405 w	416 ms	
			407 sh			
252	237	245	223	245	214	$\Delta = \nu(CO_2)_{asym} - \nu(CO_2)_{sym}$
264	265	270	240		222	

[a]Raman data.

can be assigned to the spin-forbidden $^4T_{1g} \to {}^2E_g$ transition. The position of this band precludes its assignment as the 'two-electron' spin-allowed ν_2 transition, $^4T_{1g} \to {}^4A_{2g}$, as it has been shown [13] that the ratio of the energies of the ν_2 and ν_1 transitions should lie between 2.1 and 2.2. For the present complex such an assignment would lead to an unreasonable ratio of 1.65. The spin-allowed transitions are observed as split bands, presumably because of distortion from regular octahedral symmetry, the degeneracies of the $^4T_{1g}$ states thereby being lifted. The intense charge-transfer bands observed are associated with both carboxylate and $\pi \to \pi^*$ ligand transitions. The spectral and magnetic features therefore suggest the presence of *cis*- or *trans*-octahedral MO_4N_2 arrangements for the bis(pyridine) complexes and for $Zn(O_2CCH_2CN)_2$(bipy), and *cis*- or *trans*-octahedral MO_2N_4 arrangements for $M(O_2CCH_2CN)_2$-(bipy)$_2$, (M = Mn or Co). This is in line with proposed structures for several cobalt(II) and nickel(II) halo-acetate-bis- and tetrakis-pyridine complexes [13, 23]. We therefore suggest that reaction of the cyano-acetates with the heterocyclic nitrogen donors takes place with cleavage of the metal–cyano-nitrogen bonding of the cyanoacetates and breakdown of their polymeric structures to give $M(O_2CCH_2CN)_2(py)_2$ and $Zn(O_2CCH_2CN)_2$(bipy) in which the carboxylate groups are O,O-chelating, and $M(O_2CCH_2CN)_2$-(bipy)$_2$ (M = Mn or Co) in which the carboxylate

groups are O-unidentate. Vibrational spectroscopy has been used in an attempt to justify these structural proposals (Table VII).

Evidence for the absence of cyano-nitrogen–metal bonds rests with the positions of the ν(CN) and δ(CCN) bands. The infrared and Raman ν(CN) bands are found at frequencies marginally below (up to 9 cm^{-1}) the frequency of the analogous band of sodium cyanoacetate. The weak infrared δ(CCN) bands appear within 7 cm^{-1} of the frequency of the analogous band of the sodium salt. This situation is therefore quite different to that found for the cyano-acetates themselves where ν(CN) are increased by *ca.* 20 cm^{-1} and δ(CCN) increased by *ca.* 40 cm^{-1} relative to the frequencies of the analogous bands of the sodium salt.

The $\nu(CO_2)_{asym}$, $\nu(CO_2)_{sym}$ band positions and hence Δ values for the three pyridine complexes and for $Zn(O_2CCH_2CN)_2$(bipy) are in line with expectations for the presence of chelating carboxylate groups in an octahedral structure. However, it may well have been expected for the two remaining 2,2'-bipyridyl complexes that the Δ values would be significantly greater, if, as we propose, unidentate carboxylate groups are present. The Δ values are, in fact, very similar to those of the pyridine complexes. This situation is not without precedence [13] since the Δ values of $Co(O_2CCHCl_2)_2(py)_2$ and $Co(O_2CCHCl_2)_2(py)_4$ containing chelating and unidentate

TABLE VIII. X-Ray Powder Data; d spacing, A (X = O_2CCH_2CN).

$MnX_2(py)_2$		$CoX_2(py)_2$		$ZnX_2(py)_2$		$MnX_2(bipy)_2$		$CoX_2(bipy)_2$		$ZnX_2(bipy)$	
d	I	d	I	d	I	d	I	d	I	d	I
11.7	vw	9.7	s	9.9	vs	10.5	m	10.1	vs	9.7	vs
10.7	vs	7.3	vw	8.6	w	9.2	vw	7.9	w	8.8	m
8.5	w	6.15	vs	7.3	vs	8.8	vs	7.0	vs	7.1	vs
7.7	vs	5.87	vs	5.87	vs	7.8	vs	6.2	w	5.66	vs
6.22	m	5.48	w	5.40	s	7.2	m	5.9	m	5.25	m
5.91	m	4.67	w	5.16	s	6.53	s	5.8	w	4.89	s
5.46	vw	4.28	w	4.93	s	5.56	vw	5.7	w	4.69	s
5.33	s	4.00	w	4.70	s	5.31	s	5.0	m	4.40	s
4.82	m	3.58	m	4.14	m	4.62	s	4.69	vw	4.16	vw
4.50	s	3.50	w	3.97	vs	4.51	w	4.18	vs	4.01	vw

dichloroacetate groups respectively are likewise almost identical. Even more strikingly, the Δ values of $Co(O_2CCX_3)_2(py)_4$ (X = F or Cl), are significantly smaller than those of $Co(O_2CCX_3)_2(py)_2$. It seems therefore that an assessment of Δ cannot be regarded as a universally valid means of differentiating between bidentate and unidentate modes of co-ordination for carboxylate groups in metal complexes.

Far-infrared spectra have been obtained in order to acquire some evidence in favour of either the *cis*- or *trans*-octahedral arrangements. Using the simplification that these complexes can be regarded as either *cis*-MO_4N_2 and –MO_2N_4 or *trans*-MO_4N_2 and –MO_2N_4 arrangements the number of $\nu(MO)$ and $\nu(MN)$ bands can be predicted. Thus for a *cis*-MO_4N_2 array, 4 $\nu(MO)$ + 2 $\nu(MN)$ are predicted whereas for a *trans*-MO_4N_2 array only 1 $\nu(MO)$ + 1 $\nu(MN)$ are predicted. The prediction for *cis*- and *trans*-MO_2N_4 arrays will obviously be strictly the reverse of the above. Hence a *cis*-isomer should display 6 $\nu(MO)$ + $\nu(MN)$ bands whereas only 2 $\nu(MO)$ + $\nu(MN)$ bands are expected for a *trans*-isomer. The infrared spectra (Table VII) below 300 cm^{-1} contain many bands and although definitive assignments are not possible it would therefore appear that the favoured arrangement for all the complexes is a *cis*-octahedral geometry. The tentative assignments are in line with those previously given [23] for some cobalt(II) and nickel(II) trifluoroacetate-heterocyclic nitrogen donor complexes, for which $\nu(MO)$ vibrations were placed at higher frequencies than $\nu(MN)$ vibrations. The $\nu(MN)$ frequencies are also in agreement with those given for other first-row transition metal–pyridine and –2,2'-bipyridyl complexes [24, 25]. The presence of low frequency ligand bands at ca. 420 cm^{-1} for the pyridine complexes and split bands centred at *ca.* 415 cm^{-1} for the 2,2'-bipyridyl complexes do not confuse the above assignments. The ligand bands between 1700 and 600 cm^{-1} have

been discussed many times before but as they are not diagnostically useful they will not be mentioned here.

The thermal decomposition of each complex was also studied by heating samples in air in a thermogravimetric analysis apparatus. The results will not be discussed in detail as, at the heating rate employed (4 °C per min.), each complex decomposed with simultaneous loss of ligands and cyanoacetate groups to leave the oxides previously mentioned for the uncomplexed cyanoacetates. X-ray powder photographs of the complexes contained many lines indicating a low symmetry crystal class. The results have not been subjected to further analysis by computer program, so we merely list in Table VIII the d spacings and relative intensities of the first 10 lines for each complex.

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