Structural Investigations of Metal–Nitrate Complexes. Part VI.† Crystal and Molecular Structure of Dinitratotrispyridinecadmium(II)

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The structure of the title compound has been determined by three-dimensional *X*-ray analysis from diffractometer data. The crystals are monoclinic, space group $C2/c$, with $Z = 4$ in a unit cell of dimensions $a = 12{\cdot}434$, $b = 9{\cdot}494$, $c = 17{\cdot}385$ Å, $\beta = 115{\cdot}42°$. The structure was solved by the heavy-atom method and refined by least-squares, full-matrix calculations to a R 0·084 for 1491 independent data. The molecule is monomeric and is constrained to possess crystallographic two-fold symmetry. Surrounding the cadmium are three pyridine groups (Cd–N 2·301, 2·347 Å) and two bidentate nitrate groups (Cd–O 2·444, 2·491 Å). The larger ionic radius of cadmium enables the seven-co-ordinate environment to be more regular than in the analogous Co^{II}, Cu^{II}, and Zn^{II} compounds.

As part of a study of pyridine complexes of metal(II) nitrates, the properties of $Cd(py)_3(NO_3)_2$ (py = pyridine) were reported.[1] I.r. evidence suggested that in this complex all the pyridine and nitrate groups were co-ordinated, as in other trispyridine complexes.[1-3] However, a molecular-weight determination in dimethylformamide indicated a value in excess of 7000, and on this basis it was predicted that the complex was polymeric *via* bridging nitrate groups,[1] and that the cadmium atom possessed distorted octahedral co-ordination.

$Cd(py)_3(NO_3)_2$ crystallises in the same space group as the three complexes $M(py)_3(NO_3)_2$ [4,5] (M = Co^{II}, Cu^{II}, or Zn^{II}), and with unit-cell dimensions which are similar to those of the latter three compounds. However, there is no direct equivalence between the intensities of corresponding reflexions, and although our *X*-ray analysis reveals that $Cd(py)_3(NO_3)_2$ possesses a molecular structure similar to that of the other trispyridine complexes,[5] the packing of the molecules in the crystal is in this

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† Part V, A. F. Cameron, R. H. Nuttall, and D. W. Taylor, preceding paper.

[1] T. J. Ouellette and H. M. Haendler, *Inorg. Chem.*, 1969, **8**, 1777.

[2] R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 383.

[3] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840; D. W. Herlocker and M. R. Rosenthal, *Inorg. Chim. Acta*, 1970, **4**, 501.

[4] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1971, 129.

[5] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, preceding paper.

instance distinctly different from that common to the other members of this series.

EXPERIMENTAL

Preparation of Crystals.—The complex was prepared by standard literature methods [1] and was recrystallised from ethanol–2,2-dimethoxypropane (1 : 1) containing a small amount of pyridine. The crystals were enclosed in a thin-walled glass capillary to prevent decomposition.

Crystal Data.—$C_{15}H_{15}CdN_5O_6$, $M = 473·8$, Monoclinic, $a = 12·434 \pm 0·007$, $b = 9·494 \pm 0·005$, $c = 17·385 \pm 0·009$ Å, $\beta = 115·42 \pm 0·03°$, $U = 1853$ Å^3, $D_m = 1·70$, $Z = 4$, $D_c = 1·70$, $F(000) = 944$. Space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences. Mo-K_α X-rays, $\lambda = 0·7107$ Å; μ(Mo-K_α) = 12·2 cm^{-1}.

Crystallographic Measurements.—The initial unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1·5418$ Å) and from precession photographs taken with Mo-K_α radiation. These were subsequently adjusted by least-squares refinement of θ, χ, and ϕ setting angles of twelve reflexions determined on a Hilger and Watts Y 290 diffractometer.

For the intensity measurements zirconium-filtered molybdenum radiation was used and 2698 independent reflexions were collected by use of the θ—2θ scan technique. Of these some 2082 reflexions were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz polarisation effects but no corrections for absorption were made.

Structure Determination and Refinement.—The entire structure was determined by conventional Patterson and electron-density calculations with initial phasing appropriate to the cadmium. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0·25. During these preliminary calculations an overall vibration parameter ($U_{iso} = 0·06$ Å^2) was assigned to the atoms.

The least-squares refinement of positional, thermal and scale parameters converged after 9 cycles, when R was 0·10 and R' ($= \Sigma w\Delta^2/\Sigma wF_o^2$) was 0·015. After cycle 5 a difference Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent calculations these were included with isotropic vibration parameters ($U_{iso} = 0·06$ Å^2) but were not refined. Removal of those planes for which $I \leqslant 3\sigma(I)$ left 1491 independent data and a structure factor calculation using the final parameters resulted in R 0·08 and R' 0·010 (details of the refinement are given in Table 1).

TABLE 1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
(1)—(3)	x, y, z, U_{iso} for Cd, N, O, C; one overall scale, unit weights, full matrix	0·146	0·031
(4)—(5)	x, y, z, U_{iso} for Cd, N, O, C; H atoms included but not refined, one overall scale, weighting scheme adjusted, full matrix	0·143	0·026
(6)—(9)	x, y, z, U_{ij} ($i, j = 1, 2, 3$) for Cd, N, O, C; H atoms included but not refined, small adjustments to weighting scheme, full matrix	0·108	0·015
10	planes for which I < 3σ(I) removed	0·084	0·010

In all refinement cycles, a weighting scheme of the form:

$$\sqrt{w} = \{[1 + \exp(-p_1 (\sin\theta/\lambda)^2)]/[1 + p_2|F_o| + p_3|F_o|^2]\}^{\frac{1}{2}}$$

was applied to the data. Initially the p parameters were chosen to give unit weight to all reflexions, but they were later varied as indicated by a $|F_o|$ and ($\sin\theta/\lambda$) analysis of $\Sigma w\Delta^2$. The final values are: p_1 50, p_2 0·001, and p_3 0·0001.

At the conclusion of the refinement a difference synthesis and final electron-density distribution were calculated. These revealed no errors in the structure.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 6. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20385 (4 pp., 1 microfiche).†

TABLE 2

Atom positions (fractional co-ordinates)

	x/a	y/b	z/c
Cd	0·5	0·53497(11)	0·25
C(1)	0·2878(14)	0·4667(16)	0·0662(8)
C(2)	0·1844(16)	0·4794(18)	−0·0061(9)
C(3)	0·1138(14)	0·5950(17)	−0·0143(9)
C(4)	0·1473(12)	0·6984(15)	0·0486(8)
C(5)	0·2554(11)	0·6773(14)	0·1193(8)
C(6)	0·4130(12)	0·2169(13)	0·2578(9)
C(7)	0·3135(13)	0·0691(14)	0·2584(10)
C(8)	0·5	−0·0010(17)	0·25
O(1)	0·4237(9)	0·7126(10)	0·3156(6)
O(2)	0·4025(10)	0·5003(10)	0·3474(7)
O(3)	0·3604(11)	0·6713(14)	0·4120(8)
N(1)	0·3247(9)	0·5649(10)	0·1297(6)
N(2)	0·3957(9)	0·6298(12)	0·3609(7)
N(3)	0·5	0·2878(19)	0·25

TABLE 3

(*a*) Anisotropic temperature factors (A^2) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cd	0·045	0·036	0·046	0·000	0·026	0·000
C(1)	0·080	0·064	0·048	−0·010	0·019	0·027
C(2)	0·088	0·073	0·053	0·009	0·001	0·041
C(3)	0·075	0·074	0·050	0·013	0·015	−0·024
C(4)	0·054	0·065	0·050	0·016	0·008	0·018
C(5)	0·051	0·053	0·057	0·006	0·030	0·010
C(6)	0·059	0·041	0·078	−0·003	0·067	−0·016
C(7)	0·068	0·049	0·081	0·002	0·070	−0·016
C(8)	0·077	0·038	0·059	0·000	0·017	0·000
O(1)	0·074	0·054	0·060	0·007	0·037	−0·013
O(2)	0·084	0·048	0·094	0·003	0·092	−0·002
O(3)	0·102	0·095	0·090	−0·076	0·119	−0·023
N(1)	0·049	0·046	0·047	0·009	0·032	0·017
N(2)	0·049	0·059	0·057	−0·021	0·029	−0·010
N(3)	0·074	0·038	0·059	0·000	0·044	0·000

* These are the values of U_{ij} in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$

(*b*) Mean estimated standard deviations (A^2)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cd	0·001	0·001	0·001	0·000	0·001	0·000
C	0·008	0·008	0·006	0·010	0·012	0·012
O	0·006	0·005	0·006	0·009	0·010	0·008
N	0·005	0·005	0·005	0·008	0·008	0·008

The fractional co-ordinates of all non-hydrogen atoms are given in Table 2 and the anisotropic thermal parameters in Table 3. Table 4 contains bonded distances, valence angles,

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

and intra- and inter-molecular distances. The estimated standard deviations recorded in Tables 2—4 were derived from the inverse of the least-squares, normal-equation matrix, and are best regarded as minimum values. Some molecular planes are included in Table 5.

TABLE 4

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances

Cd–O(1)	2·444(9)	C(3)–C(4)	1·393(21)
Cd–O(2)	2·491(10)	C(4)–C(5)	1·392(18)
Cd–N(1)	2·301(9)	N(3)–C(6)	1·330(15)
Cd–N(3)	2·347(14)	C(6)–C(7)	1·402(18)
N(1)–C(1)	1·365(18)	C(7)–C(8)	1·325(16)
N(1)–C(5)	1·335(15)	N(2)–O(1)	1·263(14)
C(1)–C(2)	1·363(23)	N(2)–O(2)	1·261(14)
C(2)–C(3)	1·374(22)	N(2)–O(3)	1·213(19)

(*b*) Interbond angles

O(1)–Cd–O(2)	51·3(3)	C(3)–C(4)–C(5)	116·2(12)
O(1)–Cd–O(1′)	92·8(3)	C(4)–C(5)–N(1)	123·9(12)
O(1)–Cd–O(2′)	143·9(2)	Cd–N(1)–C(1)	120·7(8)
O(1)–Cd–N(1)	86·2(3)	Cd–N(1)–C(5)	121·8(8)
O(1)–Cd–N(1′)	84·1(3)	C(1)–N(1)–C(5)	117·6(11)
O(1)–Cd–N(3)	133·6(2)	C(7)–C(6)–N(3)	120·4(12)
O(2)–Cd–O(2′)	164·8(3)	C(6)–C(7)–C(8)	120·1(13)
O(2)–Cd–N(1)	95·9(3)	C(7)–C(8)–C(7′)	119·8(12)
O(2)–Cd–N(1′)	86·9(2)	Cd–N(3)–C(6)	120·4(8)
O(2)–Cd–N(3)	82·4(2)	C(6)–N(3)–C(6′)	119·2(11)
N(1)–Cd–N(1′)	165·8(3)	Cd–O(1)–N(2)	97·4(6)
N(1)–Cd–N(3)	97·1(2)	Cd–O(2)–N(2)	95·1(7)
C(2)–C(1)–N(1)	122·8(13)	O(1)–N(2)–O(2)	115·5(11)
C(1)–C(2)–C(3)	118·3(15)	O(1)–N(2)–O(3)	122·6(11)
C(2)–C(3)–C(4)	121·3(14)	O(2)–N(2)–O(3)	121·9(12)

(*c*) Intramolecular distances <3·5 Å

Cd · · · C(1)	3·22	O(2) · · · C(1′)	3·50
Cd · · · C(5)	3·21	O(2) · · · C(6)	3·14
Cd · · · C(6)	3·23	O(2) · · · O(3)	2·16
Cd · · · N(2)	2·89	O(2) · · · N(1)	3·54
O(1) · · · C(5)	3·16	O(2) · · · N1′)	3·30
O(1) · · · O(1′)	3·54	O(2) · · · N(3)	3·19
O(1) · · · O(2)	2·14		
O(1) · · · O(3)	2·17		
O(1) · · · N(1)	3·24		
O(1) · · · N(1′)	3·18		

(*d*) Intermolecular contacts <3·65 Å

O(1) · · · C(3$^{\mathrm{I}}$)	3·42	O(3) · · · C(2$^{\mathrm{IV}}$)	3·40
O(1) · · · C(7$^{\mathrm{II}}$)	3·52	O(3) · · · C(2$^{\mathrm{V}}$)	3·51
O(1) · · · C(8$^{\mathrm{II}}$)	3·24	O(3) · · · C(4$^{\mathrm{I}}$)	3·55
O(2) · · · C(4$^{\mathrm{III}}$)	3·58	O(3) · · · C(6$^{\mathrm{V}}$)	3·44
O(3) · · · C(1$^{\mathrm{IV}}$)	3·43	O(3) · · · C(7$^{\mathrm{V}}$)	3·56
O(3) · · · C(1$^{\mathrm{V}}$)	3·47	N(2) · · · C(7$^{\mathrm{V}}$)	3·55

Roman numerals as superscripts refer to the following equivalent positions with respect to the reverence molecule at x, y, z:

I $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$
II $x, 1 + y, z$
III $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
IV $x, 1 - y, \frac{1}{2} + z$
V $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

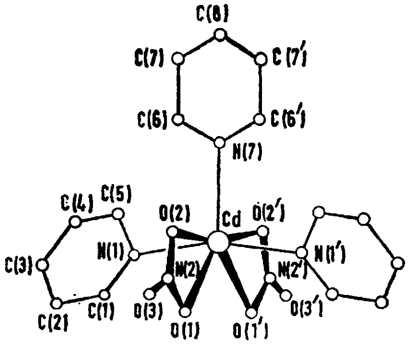

FIGURE 1 A view of the molecule along *c* showing the atomic numbering

TABLE 5

Least-squares best planes through the molecule. The equations are in the form $kX' + lY' + mZ' = n$ where X', Y', Z' are co-ordinates in Å. Distances of atoms from planes (Å) are given in square brackets

	k	*l*	*m*	*n*
Plane (1):				
O(1)—(3), N(2)	−0·9431	0·0013	−0·3325	−5·5546
[O(1) 0·004, O(2) 0·004, O(3) 0·005, N(2) −0·013, Cd −0·292]				
Plane (2):				
C(1)—(5), N(1)	0·4810	0·4914	−0·7260	4·0159
[C(1) −0·004, C(2) 0·008, C(3) −0·004, C(5) 0·009, N(1) −0·005, Cd −0·005]				
Plane (3):				
C(6)—(8), N(3)	−0·5270	−0·0014	−0·8498	−4·3869
[C(6) 0·004, C(7) −0·004, C(8) 0·002, N(3) −0·002 Cd −0·005]				

Dihedral angles between planes (°)

(1)—(2)	78	(1)—(3)	39	(2)—(3)	69

The atomic numbering scheme is shown in Figure 1 and the packing arrangement of the molecule in the unit cell is given in Figure 2.

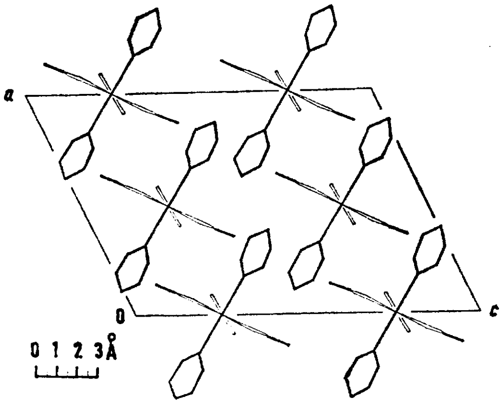

FIGURE 2 The molecular packing viewed along the *b* axis

DISCUSSION

Our analysis has revealed that crystalline Cd(py)$_3$(NO$_3$)$_2$ is monomeric, in direct contrast to the predicted polymeric nature of the complex,[1] and that the cadmium atom is surrounded by three pyridine and two bidentate nitrate groups (Figure 1). The crystallographic requirement for two-fold molecular symmetry found for the three complexes M(py)$_3$(NO$_3$)$_2$ [4,5] (M = Co$^{\mathrm{II}}$, Cu$^{\mathrm{II}}$, and Zn$^{\mathrm{II}}$), is maintained in the present case, and in this sense the molecular packing of all four compounds are similar. However, Cd(py)$_3$(NO$_3$)$_2$ is distinguished from the other three complexes by positioning of the molecules in the y direction of the crystal, and also in the spatial arrangement of the ligands about the two-fold axis, there being no obvious, nor direct, relationship between the co-ordinates of atoms in the present complex and those of the other complexes. Comparison of intermolecular distances in all four complexes does not indicate any striking changes in the efficiency of packing as a result of these differences, and indeed many of the contacts do not vary greatly. In each case, the closest approaches between molecules are either equal to or greater than the sums of the corresponding van der Waals' radii.

The largest contrast between the molecular structure of $Cd(py)_3(NO_3)_2$ and the molecular structures of the other trispyridine complexes, lies in the mode of nitrate co-ordination. In the present complex, the cadmium–oxygen distances [Cd–O(1) 2·444(9), Cd–O(2) 2·491(10) Å], although just significantly different, indicate that the nitrate groups are almost symmetrically co-ordinated, whereas the corresponding dimensions in the Co^{II}, Cu^{II}, and Zn^{II} complexes indicate distinct if differing degrees of asymmetry in the metal–nitrate bonding. Consideration of the differences in respective metal–oxygen distances in each of the Cd^{II}, Co^{II}, and Zn^{II} complexes as indicating the individual asymmetries of the nitrate co-ordination, shows that these three complexes form a well defined series [{M–O(2)} – {M–O(1)} 0·047 (Cd), 0·104 (Co), and 0·186 Å (Zn)] in which the asymmetry shows an expected increase with decreasing metal ionic radius. Thus the larger size of cadmium can more readily accommodate a regular seven-co-ordinate environment. The Cu^{II} complex is an anomalous member of the series as a result of static Jahn–Teller distortions.[5]

Although the cadmium–ligand bonds are long compared with previously recorded values for six-co-ordinate cadmium complexes,[7] the Cd–O distances are of the same order as found in the eight-co-ordinate $Cd(NO_3)_2,4H_2O$ [8] [Cd–O(NO_3) 2·44 and 2·59 Å]. A similar effect was noted in the structures of the other trispyridine complexes.[5]

If the nitrate groups are regarded as occupying single co-ordination sites [9] the structure may be described on the basis of distorted square-based pyramidal geometry. Alternatively, the seven-co-ordinate geometry may be rationalised by regarding the pyridines as occupying three corners of a square plane with the fourth corner bisecting two of the oxygens of the nitrate groups [M–O(1) and M–O(1′)]. The remaining two oxygen [O(2) and O(2′)] then occupy the sites axial to this plane. This type of description of the bonding has been used in explaining the distortions present in the complex $Cu(py)_3(NO_3)_2$.[5]

There is a polarisation effect discernible in the nitrate groups with the terminal N–O bond [1·213(19) Å] shorter than the other two [1·263(14), 1·261(14) Å]. The O–N–O angles are all distorted from 120° and the Cd–O–N angles [Cd–O(1)–N(2) 97·4(6)°, Cd–O(2)–N(2) 95·1(7)°] approach the values normally found for symmetric bidentate metal–nitrato-bonding.[10] As for the previous members of the series,[5] all the metal-bonded groups are arranged so as to minimise steric interaction.

The computations were performed on the Glasgow University KDF 9 computer using programs developed by the Glasgow group.

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