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# Structural Investigations of Metal–Nitrate Complexes. Part VII.† Crystal and Molecular Structure of Aquodinitratobis(quinoline)cadmium(II)

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The structure of the title compound has been determined by three-dimensional *X*-ray analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 11{\cdot}018 \pm 0{\cdot}005$, $b = 8{\cdot}585 \pm 0{\cdot}005$, $c = 23{\cdot}756 \pm 0{\cdot}009$ Å, $\beta = 91{\cdot}07 \pm 0{\cdot}02°$. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final *R* of 0·08 for 3697 independent reflexions. The molecule is a seven-co-ordinate monomer with non-equivalent bidentate nitrate groups. The bonding environment of the cadmium is a distorted pentagonal bipyramid, and there is a complex system of intermolecular hydrogen bonding.

QUINOLINE complexes of the type $M(quin)_2(NO_3)_2$ ($M = Co^{II}$, $Ni^{II}$, $Cu^{II}$, and $Zn^{II}$) have previously been examined,[1] and it has been suggested that they possess structures which are closely related to that of $(Me_3PO)_2Co(NO_3)_2$.[2] It might also be expected that the corresponding cadmium(II) complex would belong to this structural type, although a polymeric species involving bridging nitrato-groups is also possible. However, our attempts to prepare $Cd(quin)_2(NO_3)_2$ proved unsuccessful, and the only crystalline compound which resulted was the mono-hydrated species $Cd(quin)_2(NO_3)_2(H_2O)$. We therefore determined the crystal structure of the latter complex, not only in an effort to gain some information about the anhydrous parent compound, but also to examine the geometry of the nitrate group in the presence both of a water molecule and also of a ligand bulkier than pyridine.

## EXPERIMENTAL

*Preparation of Crystals.*—Crystals were prepared from a solution of ethanol–2,2-dimethoxypropane 1 : 1 containing stoicheiometric amounts of $Cd(NO_3)_2,4H_2O$ and quinoline, as colourless needles with the needle-axis corresponding to *b*. To avoid atmospheric decomposition in the *X*-ray beam, the crystals were enclosed in thin-walled glass tubes.

*Crystal Data.*—$C_{18}H_{16}CdN_4O_7$, $M = 512{\cdot}8$, Monoclinic, $a = 11{\cdot}018 \pm 0{\cdot}005$, $b = 8{\cdot}585 \pm 0{\cdot}005$, $c = 23{\cdot}756 \pm 0{\cdot}009$ Å, $\beta = 91{\cdot}07 \pm 0{\cdot}02°$, $U = 2247$ Å$^3$, $D_m = 1{\cdot}51$, $Z = 4$, $D_c = 1{\cdot}52$, $F(000) = 1024$, Space group $P2_1/c$ ($C^5_{2h}$, No. 14) from systematic absences. Mo-$K_\alpha$ *X*-rays, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 10{\cdot}1$ cm$^{-1}$.

*Crystallographic Measurements.*—Unit-cell parameters were initially determined from oscillation and Weissenberg photographs taken with Cu-$K_\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), and from precession photographs taken with Mo-$K_\alpha$ radiation. These were subsequently adjusted by least-squares refinement of $\theta$, $\chi$, and $\phi$ setting angles of 12 reflexions determined on a Hilger and Watts Y290 diffractometer.

For the intensity measurements, zirconium-filtered molybdenum radiation was used and 3944 reflexions were collected by use of the $\omega$—$2\theta$ scan technique. Of these, 3697 reflexions were considered observed, having $I \geqslant 1\sigma(I)$, where $\sigma$ 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 atom. Several cycles of structure-

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† Part VI, ref. 6.

[1] A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 1042.

[2] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

factor and electron-density calculations effected preliminary refinement and reduced $R$ to 0·23. During these preliminary calculations an overall isotropic 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 11 cycles, when $R$ was 0·08 and $R'$ $(= \Sigma w\Delta^2/\Sigma wF_o^2)$ was 0·011. Removal of those planes for which $I \geqslant 2\sigma(I)$ left 3029 independent data, and a structure-factor calculation using the final parameters resulted in $R$ 0·06 and $R'$ 0·008. After cycle 5, a difference-Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent cycles these were refined with isotropic temperature factors (for details of the refinement see Table 1). The refinement of anisotropic thermal parameters necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations. 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. Initially the $p$ parameters were chosen to give unit weights to all reflexions, but were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\Sigma w\Delta^2$. Final values are $p_1$ 50, $p_2$ 0·001, and $p_3$ 0·01.

TABLE 1

Course of refinement

| Cycles | Parameters refined | Final $R$ | Final $R'$ |
|---|---|---|---|
| 1—4 | $x, y, z, U_{iso}$ for Cd, N, O, C; layer scale factors, unit weights, full matrix | 0·114 | 0·0433 |
| 5—6 | $x, y, z, U_{iso}$ for Cd, N, O, C; layer scale factors, weighting scheme adjusted, full matrix | 0·103 | 0·0372 |
| 7—8 | $x, y, z, U_{iso}$ for Cd, N, O, C, H; one overall scale factor, weighting scheme adjusted, full matrix | 0·100 | 0·0298 |
| 9—11 | $x, y, z, U_{ij}$ ($i, j$ = 1,2,3) for Cd, N, O, C; $x, y, z, U_{iso}$ for H; small adjustments to weighting scheme, block-diagonal approximation to normal-equation matrix | 0·078 | 0·0112 |
| 12 | Planes having $I \leqslant 2\sigma(I)$ removed | 0·060 | 0·0081 |

At the conclusion of the refinement a difference-Fourier synthesis and final electron-density distribution were calculated. These revealed no errors in the structure. In all structure-factor calculations, atomic scattering factors were taken from ref. 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20759 (5 pp., 1 microfiche).*

Fractional co-ordinates of all non-hydrogen atoms are given in Table 2 and anisotropic thermal parameters in Table 3. The positions of the hydrogen atoms and their isotropic thermal parameters are given in Table 4.

Table 5 contains bonded distances, valence angles, and intra- and inter-molecular distances. The estimated standard deviations recorded in Tables 2—5 were derived from the inverse of the least-squares normal-equation matrix, and are best regarded as minimum values. A number of planes were calculated for portions of the molecular framework (Table 6).

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

TABLE 2

Atom positions (fractional co-ordinates)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cd | 0·13619(5) | 0·05436(6) | 0·31853(2) |
| C(1) | 0·0118(7) | −0·2073(8) | 0·3771(3) |
| C(2) | 0·0704(8) | −0·3047(9) | 0·4157(4) |
| C(3) | 0·0326(8) | −0·2985(9) | 0·4696(4) |
| C(4) | 0·0666(8) | −0·1955(10) | 0·4871(3) |
| C(5) | 0·1098(9) | −0·1855(10) | 0·5430(4) |
| C(6) | 0·2030(10) | −0·0876(12) | 0·5550(5) |
| C(7) | 0·2574(9) | −0·0007(11) | 0·5142(4) |
| C(8) | 0·2173(8) | −0·0069(10) | 0·4596(4) |
| C(9) | 0·1197(7) | −0·1042(9) | 0·4447(3) |
| C(10) | 0·3969(8) | 0·1969(9) | 0·3055(4) |
| C(11) | 0·5251(8) | 0·2216(11) | 0·2993(4) |
| C(12) | 0·6004(8) | 0·0939(12) | 0·3096(4) |
| C(13) | 0·5522(8) | 0·0476(9) | 0·3260(4) |
| C(14) | 0·6250(8) | 0·1808(12) | 0·3369(5) |
| C(15) | 0·5746(10) | 0·3159(11) | 0·3528(5) |
| C(16) | 0·4489(9) | 0·3312(10) | 0·3583(5) |
| C(17) | 0·3725(8) | 0·2053(9) | 0·3474(4) |
| C(18) | 0·4238(8) | 0·0594(9) | 0·3311(4) |
| O(1) | 0·1683(6) | 0·0736(7) | 0·2152(3) |
| O(2) | 0·1517(5) | 0·1564(7) | 0·2508(2) |
| O(3) | 0·1825(7) | 0·1299(9) | 0·1612(3) |
| O(4) | 0·1203(7) | 0·3261(7) | 0·2972(3) |
| O(5) | 0·1453(7) | 0·2869(9) | 0·3859(3) |
| O(6) | 0·1521(8) | 0·5226(9) | 0·3526(4) |
| O(7) | 0·0663(6) | 0·0536(7) | 0·2862(3) |
| N(1) | 0·0769(6) | 0·1093(8) | 0·3893(3) |
| N(2) | 0·3475(7) | 0·0648(8) | 0·3198(3) |
| N(3) | 0·1674(6) | 0·0685(7) | 0·2075(3) |
| N(4) | 0·1394(7) | 0·3837(9) | 0·3465(3) |

TABLE 3

(*a*) Anisotropic temperature factors (Å$^2$ × 10$^3$)*

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{32}$ | $2U_{31}$ | $2U_{12}$ |
|---|---|---|---|---|---|---|
| Cd | 37 | 37 | 37 | 2 | −2 | −3 |
| C(1) | 50 | 26 | 43 | 11 | −10 | 4 |
| C(2) | 47 | 41 | 64 | 2 | 9 | −12 |
| C(3) | 51 | 56 | 48 | 30 | 35 | 1 |
| C(4) | 53 | 57 | 33 | 23 | 16 | 35 |
| C(5) | 71 | 62 | 44 | 1 | −13 | 20 |
| C(6) | 70 | 98 | 44 | −13 | −24 | 45 |
| C(7) | 57 | 77 | 45 | −8 | −37 | 12 |
| C(8) | 45 | 51 | 53 | −6 | −16 | −2 |
| C(9) | 42 | 43 | 38 | −2 | −2 | 20 |
| C(10) | 48 | 59 | 47 | 7 | −16 | 4 |
| C(11) | 48 | 62 | 65 | 1 | 13 | −35 |
| C(12) | 33 | 78 | 58 | −2 | −1 | −17 |
| C(13) | 42 | 69 | 37 | −24 | 11 | −1 |
| C(14) | 44 | 82 | 63 | −42 | −12 | 23 |
| C(15) | 67 | 56 | 69 | −3 | −6 | 45 |
| C(16) | 59 | 58 | 68 | 17 | 11 | 37 |
| C(17) | 47 | 40 | 53 | 19 | 4 | 13 |
| C(18) | 41 | 56 | 39 | 4 | 8 | 3 |
| O(1) | 53 | 54 | 52 | 2 | −4 | −3 |
| O(2) | 50 | 38 | 48 | 9 | −8 | −15 |
| O(3) | 95 | 63 | 45 | −22 | 7 | 2 |
| O(4) | 66 | 43 | 66 | −16 | −30 | 3 |
| O(5) | 70 | 69 | 63 | 9 | 19 | 23 |
| O(6) | 94 | 38 | 99 | −41 | −23 | 19 |
| O(7) | 43 | 40 | 71 | 1 | −5 | 8 |
| N(1) | 38 | 34 | 32 | 1 | 4 | −5 |
| N(2) | 44 | 48 | 39 | 14 | 4 | −14 |
| N(3) | 38 | 41 | 32 | −5 | −10 | −2 |
| N(4) | 48 | 34 | 67 | −7 | 13 | 4 |

(*b*) Mean estimated standard deviations (Å$^2$ × 10$^3$)

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{32}$ | $2U_{31}$ | $2U_{12}$ |
|---|---|---|---|---|---|---|
| Cd | 1 | 1 | 1 | 1 | 1 | 1 |
| C | 4 | 4 | 5 | 8 | 8 | 8 |
| O | 4 | 3 | 3 | 6 | 7 | 6 |
| N | 3 | 3 | 3 | 6 | 6 | 5 |

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

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full-size copies).

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

TABLE 4

Hydrogen positions * (fractional co-ordinates) and isotropic temperature factors (Å²)

| | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|
| H(1)[C(1)] | 0·030(12) | 0·209(15) | 0·346(5) | 0·06(5) |
| H(2)[C(2)] | 0·138(12) | 0·396(17) | 3·407(6) | 0·07(3) |
| H(3)[C(3)] | 0·062(12) | 0·354(16) | 0·491(6) | 0·06(3) |
| H(5)[C(5)] | 0·081(12) | 0·286(17) | 0·558(6) | 0·07(3) |
| H(6)[C(6)] | 0·225(14) | 0·084(15) | 0·597(6) | 0·07(4) |
| H(7)[C(7)] | 0·323(14) | 0·066(15) | 0·519(6) | 0·03(4) |
| H(8)[C(8)] | 0·241(13) | 0·064(14) | 0·443(6) | 0·05(4) |
| H(10)[C(10)] | 0·345(12) | 0·281(16) | 0·294(5) | 0·05(3) |
| H(11)[C(11)] | 0·549(12) | 0·310(15) | 0·289(5) | 0·03(4) |
| H(12)[C(12)] | 0·694(14) | 0·077(17) | 0·304(6) | 0·05(4) |
| H(14)[C(14)] | 0·723(12) | 0·171(17) | 0·330(6) | 0·06(4) |
| H(15)[C(15)] | 0·635(13) | 0·392(16) | 0·357(6) | 0·06(4) |
| H(16)[C(16)] | 0·429(13) | 0·443(14) | 0·370(6) | 0·07(4) |
| H(17)[C(17)] | 0·290(12) | 0·235(16) | 0·361(6) | 0·07(4) |
| H(19)[O(7)] | 0·065(8) | 0·011(10) | 0·256(4) | 0·04(2) |
| H(20)[O(7)] | 0·087(9) | 0·133(9) | 0·274(4) | 0·10(2) |

* Hydrogens are bonded to atoms shown in square brackets.

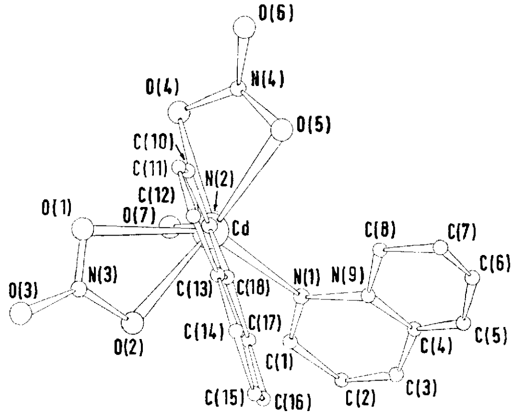

FIGURE 1 A view of the molecule along *a* showing the atomic numbering

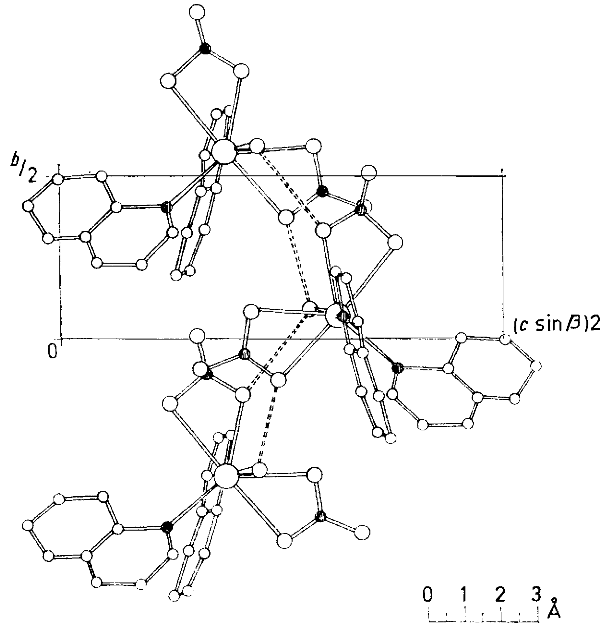

FIGURE 2 The structure viewed along *a* showing the hydrogen bonding

TABLE 5

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

(*a*) Bonded distances (Å)

| | | | |
|---|---|---|---|
| Cd–O(1) | 2·492(7) | C(10)–N(2) | 1·305(11) |
| Cd–O(2) | 2·430(8) | C(10)–C(11) | 1·439(13) |
| Cd–O(4) | 2·393(7) | C(11)–C(12) | 1·394(11) |
| Cd–O(5) | 2·559(9) | C(12)–C(13) | 1·385(14) |
| Cd–O(7) | 2·346(7) | C(13)–C(14) | 1·417(14) |
| Cd–N(1) | 2·296(7) | C(13)–C(18) | 1·426(13) |
| Cd–N(2) | 2·330(7) | C(14)–C(15) | 1·343(15) |
| C(1)–N(1) | 1·318(10) | C(15)–C(16) | 1·400(15) |
| C(1)–C(2) | 1·407(12) | C(16)–C(17) | 1·391(13) |
| C(2)–C(3) | 1·340(14) | C(17)–C(18) | 1·431(12) |
| C(3)–C(4) | 1·460(13) | C(18)–N(2) | 1·382(11) |
| C(4)–C(5) | 1·406(13) | N(3)–O(1) | 1·233(10) |
| C(4)–C(9) | 1·411(12) | N(3)–O(2) | 1·289(11) |
| C(5)–C(6) | 1·353(15) | N(3)–O(3) | 1·235(11) |
| C(6)–C(7) | 1·370(15) | N(4)–O(4) | 1·287(10) |
| C(7)–C(8) | 1·363(15) | N(4)–O(5) | 1·252(11) |
| C(8)–C(9) | 1·402(13) | N(4)–O(6) | 1·209(8) |
| C(9)–N(1) | 1·389(11) | Mean C–H | 0·95 |
| | | Mean O–H | 0·85 |

(*b*) Interbond angles (°)

| | | | |
|---|---|---|---|
| O(1)–Cd–O(2) | 52·0(2) | C(6)–C(7)–C(8) | 120·9(9) |
| O(1)–Cd–O(4) | 74·8(2) | C(7)–C(8)–C(9) | 119·8(8) |
| O(1)–Cd–O(5) | 124·0(2) | C(8)–C(9)–C(4) | 118·4(8) |
| O(1)–Cd–O(7) | 80·2(2) | C(4)–C(9)–N(1) | 121·4(8) |
| O(1)–Cd–N(1) | 144·1(2) | C(8)–C(9)–N(1) | 120·2(8) |
| O(1)–Cd–N(2) | 81·4(2) | Cd–N(2)–C(10) | 116·8(8) |
| O(2)–Cd–O(4) | 126·2(3) | Cd–N(2)–C(18) | 125·3(5) |
| O(2)–Cd–O(5) | 173·0(3) | C(10)–N(2)–C(18) | 117·8(7) |
| O(2)–Cd–O(7) | 81·9(2) | C(11)–C(10)–N(2) | 124·7(8) |
| O(2)–Cd–N(1) | 93·1(3) | C(10–C(11)–C(12) | 116·7(9) |
| O(2)–Cd–N(2) | 87·4(2) | C(11)–C(12)–C(13) | 120·6(9) |
| O(4)–Cd–O(5) | 51·3(3) | C(12)–C(13)–C(14) | 122·7(9) |
| O(4)–Cd–O(7) | 82·4(3) | C(12)–C(13)–C(18) | 118·2(8) |
| O(4)–Cd–N(1) | 137·0(3) | C(14)–C(13)–C(18) | 119·1(8) |
| O(4)–Cd–N(2) | 92·0(2) | C(13)–C(14)–C(15) | 120·8(9) |
| O(5)–Cd–O(7) | 103·5(3) | C(14)–C(15)–C(16) | 121·5(9) |
| O(5)–Cd–N(1) | 91·6(3) | C(15)–C(16)–C(17) | 120·4(9) |
| O(5)–Cd–N(2) | 86·2(3) | C(16)–C(17)–C(18) | 119·3(8) |
| O(7)–Cd–N(1) | 87·5(2) | C(17)–C(18)–C(13) | 119·8(8) |
| O(7)–Cd–N(2) | 161·5(2) | C(13)–C(18)–N(2) | 122·0(7) |
| N(1)–Cd–N(2) | 108·2(3) | C(17–C(18)–N(2) | 119·1(8) |
| Cd–N(1)–C(1) | 116·7(5) | Cd–O(1)–N(3) | 94·5(5) |
| Cd–N(1)–C(9) | 125·3(6) | Cd–O(2)–N(3) | 96·0(5) |
| C(1)–N(1)–C(9) | 117·7(7) | Cd–O(4)–N(4) | 99·9(5) |
| C(2)–C(1)–N(1) | 125·7(8) | Cd–O(5)–N(4) | 92·9(6) |
| C(1)–C(2)–C(3) | 117·5(8) | O(1)–N(3)–O(2) | 117·6(8) |
| C(2)–C(3)–C(4) | 120·8(8) | O(1)–N(3)–O(3) | 123·6(8) |
| C(3)–C(4)–C(5) | 122·9(8) | O(2)–N(3)–O(3) | 118·9(8) |
| C(3)–C(4)–C(9) | 116·9(7) | O(4)–N(4)–O(5) | 115·5(7) |
| C(5)–C(4)–C(9) | 120·2(8) | O(4)–N(4)–O(6) | 120·4(8) |
| C(4)–C(5)–C(6) | 118·6(9) | O(5)–N(4)–O(6) | 124·1(8) |
| C(5)–C(6)–C(7) | 122·0(9) | H(19)–O(7)–H(20) | 104(8) |

| | |
|---|---|
| Mean C–C–H | 119 |
| Mean N–C–H | 116 |
| O(4)′ · · · O(7) · · · O(2″) | 109·2(8) |

(*c*) Intramolecular non-bonded distances (Å) for non-hydrogen atoms

| | | | |
|---|---|---|---|
| Cd · · · C(1) | 3·12 | O(2) · · · O(7) | 3·13 |
| Cd · · · C(8) | 3·49 | O(2) · · · N(1) | 3·43 |
| Cd · · · C(9) | 3·30 | O(2) · · · N(2) | 3·29 |
| Cd · · · C(10) | 3·14 | O(4) · · · C(10) | 3·25 |
| Cd · · · C(17) | 3·49 | O(4) · · · O(7) | 3·12 |
| Cd · · · C(18) | 3·32 | O(4) · · · N(2) | 3·40 |
| Cd · · · N(3) | 2·87 | O(5) · · · C(8) | 3·16 |
| Cd · · · N(4) | 2·90 | O(5) · · · C(10) | 3·48 |
| O(1) · · · O(4) | 2·97 | O(5) · · · N(1) | 3·49 |
| O(1) · · · O(7) | 3·12 | O(5) · · · N(2) | 3·35 |
| O(1) · · · N(2) | 3·15 | O(7) · · · C(1) | 3·16 |
| O(2) · · · C(17) | 3·34 | O(7) · · · N(1) | 3·21 |
| N(2) · · · N(3) | 3·49 | O(7) · · · N(3) | 3·38 |

TABLE 5 (*continued*)

(*d*) Intermolecular contacts $<3{\cdot}45$ Å including those involved in hydrogen bonding

| | | | |
|---|---|---|---|
| $O(1) \cdots C(1^{I})$ | 3·34 | $O(4) \cdots O(7^{I})$ | 2·84 |
| $O(1) \cdots C(2^{I})$ | 3·44 | $O(4) \cdots N(3^{I})$ | 3·30 |
| $O(1) \cdots C(14^{II})$ | 3·36 | $O(4) \cdots H(19^{I})$ | 1·97 |
| $O(1) \cdots C(15^{II})$ | 3·42 | $O(5) \cdots C(5^{VI})$ | 3·42 |
| $O(2) \cdots O(4^{III})$ | 3·19 | $O(6) \cdots C(1^{VII})$ | 3·00 |
| $O(2) \cdots O(7^{III})$ | 2·80 | $O(6) \cdots C(2^{VII})$ | 3·26 |
| $O(2) \cdots H(20^{III})$ | 2·03 | $O(6) \cdots C(17^{VII})$ | 3·37 |
| $O(3) \cdots C(5^{IV})$ | 3·31 | $O(6) \cdots O(7^{I})$ | 3·42 |
| $O(3) \cdots C(12^{V})$ | 3·43 | $O(6) \cdots N(1^{VII})$ | 3·39 |
| $O(3) \cdots O(7^{III})$ | 3·26 | $O(7) \cdots N(3^{I})$ | 3·43 |

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

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

TABLE 6

Least-squares best planes through the molecule. The equations are in the form $kX' + lY' + mZ' = n$, where $X'$, $Y'$, and $Z'$ are co-ordinates in Å with respect to the orthogonalised axial system *a*, *b*, *c* sin β. Distances of atoms from planes (Å) are given in square brackets

| | *k* | *l* | *m* | *n* |
|---|---|---|---|---|
| Plane (1): | | | | |
| C(1)–(9), N(1) | 0·6514 | −0·7341 | −0·1916 | −0·4986 |
| [C(1) 0·003, C(2) 0·018, C(3) 0·007, C(4) −0·006, C(5) −0·012, C(6) −0·011, C(7) 0·018, C(8) 0·017, C(9) −0·005, N(1) −0·030, Cd −0·311] | | | | |
| Plane (2): | | | | |
| C(10)–(18), N(2) | −0·0796 | −0·2728 | −0·9588 | −7·6850 |
| [C(10) −0·004, C(11) −0·009, C(12) 0·005, C(13) −0·004, C(14) 0·010, C(15) −0·002, C(16) −0·007, C(17) 0·001, C(18) −0·004, N(2) 0·014, Cd 0·210] | | | | |
| Plane (3): | | | | |
| O(1)–(3), N(3) | −0·9877 | 0·0251 | −0·1542 | −2·5963 |
| [O(1) −0·002, O(2) −0·002, O(3) −0·002, N(3) 0·005, Cd − 0·036] | | | | |
| Plane (4): | | | | |
| O(4)–(6), N(4) | 0·9852 | −0·0926 | −0·1440 | 0·0318 |
| [O(4) 0·002, O(5) 0·002, O(6) 0·002, N(4) −0·005, Cd 0·318] | | | | |

Dihedral angles (°) between planes

| | | | |
|---|---|---|---|
| Plane (1)–(2) | 71 | Plane (2)–(3) | 77 |
| Plane (1)–(3) | 51 | Plane (2)–(4) | 85 |
| Plane (1)–(4) | 43 | Plane (3)–(4) | 18 |

## DISCUSSION

Our analysis has revealed a seven-co-ordinate monomeric structure in which the cadmium atom is surrounded by two non-equivalent, but bidentate nitrate groups, by two quinoline molecules, and by a water molecule (Figure 1). While one of the nitrate groups is almost symmetrically bidentate, the other shows slight, but significant asymmetry [$\{M{-}O(5)\}{-}\{M{-}O(4)\} = \delta = 0{\cdot}17$ Å], which is of the same order as that observed in $Cd(NO_3)_2(H_2O)_4$ [$\delta = 0{\cdot}14$ Å] [4] and in $Zn(py)_3(NO_3)_2$ [$\delta = 0{\cdot}19$ Å].[5] The cadmium–oxygen [$Cd{-}O(NO_3)$ 2·393—2·559, $Cd{-}O(H_2O)$ 2·346(7) Å] and cadmium–nitrogen [Cd–N 2·296(7), 2·330(7) Å] distances are in accord with those values previously reported for seven- and eight-co-ordinate cadmium complexes,[6-8] although they are slightly longer than those distances normally found in four-, five-, and six-co-ordinate cadmium(II) complexes.[7] Such lengthening may be explained on the basis of the increased co-ordination number of the cadmium.[4-6]

The stereochemistry of the cadmium atom may be described in a number of ways. One approach is to consider the distortions from pentagonal bipyramidal geometry. In this case the axial sites are occupied by the oxygen of the water [O(7)] and by the nitrogen of one of the quinoline molecules [N(2)], while the equatorial plane contains the nitrogen of the remaining quinoline molecule [N(1)], and the oxygens of the two nitrato-groups [O(1), O(2), O(4), and O(5)]. These last four oxygen atoms are virtually coplanar with the cadmium, although N(1) is displaced 0·88 Å from this plane (Table 6), the displacement being away from the axial quinoline function. The angular distortions within the equatorial plane are shown in Figure 3. Since the angles made by the co-ordinated oxygens of each nitrate group at the cadmium atom are restricted by the nitrate geometry to values *ca.* 52°, there is a concomitant expansion of the other angles, the largest increases from the ideal value of 72° being observed in those angles involving the nitrogen atom N(1) [*e.g.* O(2)–Cd–N(1) 93·1(3)°]. The atoms N(3) and O(7) are distorted from

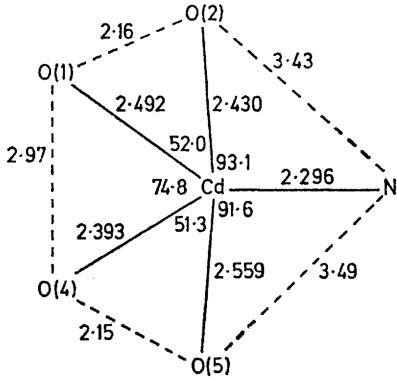

FIGURE 3 A diagrammatic representation of the equatorial plane of the pentagonal bipyramidal geometry of the molecule, showing the distortions from ideal geometry; distances in Å, angles in deg. Deviations of angles between equatorial atoms axial atoms from 90°:

| | X–Cd–N(2) | X–Cd–O(7) |
|---|---|---|
| N(1) | 108·2 | 87·5 |
| O(2) | 87·4 | 81·9 |
| O(1) | 81·4 | 80·2 |
| O(4) | 92·0 | 82·4 |
| O(5) | 86·2 | 103·5 |

Deviation of angle at cadmium atom from 180°:
N(2)–Cd–O(7) 161·5°

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ideal axial geometry such that the angle N(3)–Cd–O(7) is 161·5(2)°. Such distortions may possibly be explained in terms of the steric interactions of the quinoline ligands.

An alternative approach is to compare the geometry of the complex with the pseudotetrahedral geometry of $(Me_3PO)_2Co(NO_3)_2$,[2] since it has been predicted [1] that the anhydrous complexes $M(quin)_2(NO_3)_2$ ($M = Co^{II}$, $Ni^{II}$, $Cu^{II}$, and $Zn^{II}$) should belong to this structural class. If the present complex is regarded as a hydrated variant of this structural type, then the nitrate groups and quinoline moieties may be considered to be arranged in a pseudotetrahedral fashion around the cadmium atom, with the water molecule co-ordinating on that side of the cadmium least affected by the steric bulk of the quinoline molecules. Although this picture is fairly arbitrary, it does reflect the increase in co-ordination from Zn to Cd, since, in the four-co-ordinate pseudo-tetrahedral structure of $Zn(py)_2(NO_3)_2$,[9] the nitrate groups are unidentate in contrast to the bidentate nature of the nitrate groups of the present complex.

In discussing the internal geometry of the complex, it must be borne in mind, however, that there is an extensive network of intermolecular hydrogen bonding involving the co-ordinated water molecule and both nitrate groups. Each water molecule closely approaches two oxygen atoms, one from each of two different nitrate groups of different molecules [see Figure 2], the O · · · O distances being 2·80 Å and 2·84 Å, and the O(4′) · · · O(7) · · · O(2″) angle having a value of 109·2°. Unlike the hydrogen bonding in $Ni(py)_2(NO_3)_2(H_2O)_2$,[10] which involves the terminal oxygens of the nitrate groups, in the present case it is the metal-bonded oxygen atoms of the nitrate groups which are involved in the interactions with the water molecule.

The internal dimensions of the nitrate groups are slightly different. The nitrate group [N(4), O(4)—(6)] which shows the greatest asymmetry in its bonding to the cadmium atom, exhibits the expected [11] order of bond lengths, with the N(4)–O(4) bond [1·287(10) Å; adjacent to the shorter Cd–O(4) 2·393(7) Å bond] longer than the N(4)–O(5) bond [1·252(11) Å; adjacent to the longer Cd–O(5) 2·559(9) Å bond] and with the terminal N(4)–O(6) bond [1·209(8) Å] being the shortest. However, in the more symmetric nitrate group [N(3), O(1)—(3)] although the N(3)–O(2) bond [1·289(11) Å] is associated with the (slightly) shorter Cd–O(2) bond [2·430(8) Å] the N(3)–O(1) [1·233(10) Å] and N(3)–O(3) [1·235(11) Å] distances are experimentally identical. It may be relevant, however, that the oxygen atoms O(4) and O(2) of each nitrate group which are involved in the longest N–O bonding, are also those oxygens which participate in the intermolecular hydrogen bonding.

The internal dimensions of the quinoline ring systems are in accord with literature values.[8,12] Although both ligands are planar, in neither case is the cadmium atom coplanar with the rings (Table 6). This may be expected to arise from the stereochemical considerations of packing bulky ligands around the cadmium atom. The dihedral angle between the quinoline planes is 71°.

Computations were performed on the Glasgow University KDF 9 computer, with programs developed by the Glasgow Group.

[3/639 *Received, 27th March*, 1973]

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