Structural Investigations of Metal–Nitrate Complexes. Part V.† Crystal and Molecular Structures of Dinitratotris(pyridine)-cobalt(II), -copper(II), and -zinc(II)

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The structures of the complexes $M(C_5H_5N)_3(NO_3)_2$ [M = Co^{II} (I), Cu^{II} (II), and Zn^{II} (III)] have been determined by three-dimensional *X*-ray analyses. The crystals in each case are monoclinic, space group *C*2/*c*, with *Z* = 4 in unit cells of dimensions: (I), *a* = 12·584, *b* = 9·435, *c* = 16·327 Å, β = 109·48°; (II) *a* = 12·783, *b* = 9·199, *c* = 16·055 Å, β = 108·35°; and (III) *a* = 12·60, *b* = 9·40, *c* = 16·27 Å, β = 108·9°. The structures were solved by the heavy-atom method and refined by least-squares, full-matrix calculations to final *R* values of (I) 0·07 (1104 data), (II) 0·08 (1138 data), and (III) 0·11 (1020 data). The overall molecular geometries of the complexes are similar with the three pyridine and two nitrate groups co-ordinated to the metal in monomeric structures. The crystal packings are almost identical but the degree of asymmetry of the nitrato-co-ordination increases as Co < Zn ≪ Cu. Consideration of the stereochemistries suggest that the large distortions present in the copper complex are a result of the static Jahn–Teller effect.

THE structures of complexes of general formula $M(py)_3(NO_3)_2$ (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}; py = pyridine) have been the subject of considerable speculation. $Zn(py)_3(NO_3)_2$ Has been examined [1-3] by spectroscopic techniques, and although an octahedral structure with bridging nitrato-groups was suggested [1] the possibility of the tetranitrato-ionic structure $\{[Zn(py)_6]^{2+}[Zn(NO_3)_4]^{2-}\}$ was not excluded. $Co(py)_3(NO_3)_2$ Has been studied both in the crystalline state [2-5] and in solution,[4,5] and in the latter work it was concluded that the most likely structure was octahedral with uni- and bi-dentate nitrate groups. The structure of $Ni(py)_3(NO_3)_2$ was also thought to be of this type.[4,6] The electronic spectra of the cobalt and nickel complexes did not support the existence of tetranitrato ionic species for these two compounds.[4-6]

The existence of the complex $Cu(py)_3(NO_3)_2$ was in some doubt, since, despite previous reports of its preparation,[7,8] no evidence could be found for this phase in a thermal decomposition curve for $Cu(py)_4(NO_3)_2$.[9] It was concluded [9] that the previously prepared material was in fact a mixture of $Cu(py)_2(NO_3)_2$ and $Cu(py)_4(NO_3)_2$. Although spectroscopic details were subsequently reported for $Cu(py)_3(NO_3)_2$,[2,3] no structure was postulated for this complex.

To resolve some of these structural ambiguities, we have examined the complexes $M(py)_3(NO_3)_2$ (M = Co^{II}, Cu^{II}, and Zn^{II} [10]) by three-dimensional *X*-ray diffraction techniques. From unit-cell dimensions and comparison of the intensities of equivalent reflexions obtained from Weissenberg photographs, it was concluded that all three complexes were apparently isomorphous. The surprising nature of this result, partucularly for the copper complex, led us to determine independently the complete structure of each species. The results of the three separate analyses reveal that despite closely similar packing arrangements, there are significant detailed differences in the molecular geometries of the three complexes which might otherwise have been overlooked had the compounds been considered to be formally isomorphous.

EXPERIMENTAL

Preparation of Crystals.—All three complexes were prepared by methods which have previously been described.[1,3-5] Crystals were obtained in each case from 1 : 1 ethanol–2,2-dimethoxypropane solutions containing a small amount of pyridine. To avoid atmospheric decomposition, the crystals were enclosed in thin-walled, glass tubes.

Crystal Data.—(I), $C_{15}H_{15}CoN_5O_6$, *M* = 420·3, Monoclinic, *a* = 12·584 ± 0·005, *b* = 9·435 ± 0·004, *c* = 16·327

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[9] R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 379.

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

$\pm$ 0·006 Å, β = 109·48 $\pm$ 0·05°, U = 1828 Å^3, D_m = 1·51, Z = 4, D_c = 1·53, $F(000)$ = 860. Space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences. Mo-K_α X-Rays, λ = 0·7107 Å; μ(Mo-K_α) = 10·24 cm^{-1}.

(II) $C_{15}H_{15}ZnN_5O_6$, M = 426·7, Monoclinic, a = 12·60 $\pm$ 0·03, b = 9·40 $\pm$ 0·03, c = 16·27 $\pm$ 0·03 Å, β = 108·9 $\pm$ 0·2°, U = 1823 Å^2, D_m = 1·55, Z = 4, D_c = 1·55, $F(000)$ = 872. Space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences. Cu-K_α X-Rays, λ = 1·5418 Å, μ(Cu-K_α) = 23·2 cm^{-1}.

(III) $C_{15}H_{15}CuN_5O_6$, M = 424·9, Monoclinic, a = 12·783 $\pm$ 0·006, b = 9·199 $\pm$ 0·005, c = 16·055 $\pm$ 0·008 Å, β = 108·35 $\pm$ 0·03°, U = 1792 Å^3, D_m = 1·63, Z = 4, D_c = 1·66, $F(000)$ = 868. Space group $C2/c$ (C^6_{2h}, No. 15) systematic absences, Mo-K_α X-rays, λ = 0·7107 Å; μ(Mo-K_α) = 13·8 cm^{-1}.

Crystallographic Measurements.—The unit-cell parameters for all three complexes were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation (λ = 1·5418 Å), and from precession photographs taken with Mo-K_α (λ = 0·7107 Å) radiation.

$Co(py)_3(NO_3)_2$ (I) *and* $Cu(py)_3(NO_3)_2$ (II). The preliminary unit-cell dimensions were adjusted by least-squares analysis of θ, χ, and ϕ setting angles of twelve reflexions recorded on a Hilger and Watts Y 290 four-circle diffractometer.

For the intensity measurements zirconium-filtered molybdenum radiation was used and for the cobalt complex 2161 independent reflexions were collected (1578 for the copper complex) by use of the θ—2θ scan technique. Of these some 1849 reflexions for the cobalt complex (1466 for Cu) were considered observed using the criteria $I \leqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

$Zn(py)_3(NO_3)_2$, (III). A small crystal was mounted about b and 1020 independent reflexions from the reciprocal-lattice nets $h0$—$8l$ were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique, and were estimated visually by comparison with a calibrated strip. After correction for Lorentz, polarisation, and rotation factors, the structure amplitudes were placed on an overall scale by comparison with values obtained from the $hk0$ reciprocal-lattice net recorded by precession methods. Unobserved reflexions were not included in the calculations and absorption corrections were not applied.

Structure Determination and Refinement.—(III) The structure of the zinc complex was solved by conventional Patterson and electron-density calculations with initial phasing based on the zinc atom, and assuming the validity of space group $C2/c$.* Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0·19. An overall isotropic vibration parameter, U_{iso} (0·06 Å^2) was assigned to all atoms.

The parameters obtained at the end of the refinement for the zinc complex were used for $Co(py)_3(NO_3)_2$ and $Cu(py)_3(NO_3)_2$ and several cycles of structure-factor and electron-density calculations reduced R to 0·25 (for Co) and 0·20 (for Cu).

For $Zn(py)_3(NO_3)_2$, the correctness of the space-group choice was examined by a trial refinement in space group Cc which converged when R was 0·10 but revealed disturbing discrepancies in bond lengths, in particular an aromatic C–C bond distance of 1·73 Å. In comparison, refinement in space group $C2/c$ by full-matrix least-squares converged after 8 cycles with R 0·11 and R' ($=\Sigma w\Delta^2/\Sigma wF_o^2$) 0·023. The resulting molecular geometry showed none of the anomalies produced by the previous refinement, thus justifying our choice of the latter space group.

(I) *and* (II). Statistical analyses of the data for (I) and (II) also favoured the centrosymmetric space group and refinement in $C2/c$ by full-matrix least-squares converged after 8 cycles in each case with R 0·12 and R' 0·018 for Co, and R 0·11 and R' 0·021 for Cu. Removal of those planes for which $I \leqslant 2\sigma(I)$ left 1104 (Co) and 1138 (Cu) independent data, and structure-factor calculations using the final parameters resulted in R 0·07, R' 0·008 (Co), and R 0·08, R' 0·011 (Cu). (Details of the refinements are given in Table 1).

TABLE 1

Course of refinement

Complex	Cycles	Parameters refined	Final R	Final R'
	(1)—(3)	x, y, z, U_{iso} for M, N, O, C; layer scale-factors for Zn, overall scale for Co and Cu, unit weights, full matrix		
Zn			0·141	0·034
Co			0·139	0·041
Cu			0·156	0·033
	(4)—(5)	x, y, z, U_{iso} for M, N, O, C; one overall scale, weighting scheme adjusted, full matrix		
Zn			0·135	0·028
Co			0·136	0·025
Cu			0·140	0·026
	(6)—(8)	x, y, z, U_{ij} $(i,j = 1, 2, 3)$, for M, N, O, C; small adjustments to weighting scheme, full matrix		
Zn			0·111	0·023
Co			0·123	0·018
Cu			0·114	0·021
	(9)	Planes for which $I \leqslant 2\sigma(I)$ removed		
Co			0·072	0·008
Cu			0·081	0·011

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 they were varied in later cycles as indicated by an $[|F_o|$ and $(\sin\theta/\lambda)]$ analysis of $\Sigma w\Delta^2$. The final values are: (III), p_1 50, p_2 0·1, and p_3 0·0001; (I), p_1 100, p_2 0·01, and p_3 0·0001; and (II) p_1 50, p_2 0·001, and p_3 0·0001.

At the conclusion of the refinement, difference syntheses and final electron-density distributions were calculated. These revealed no errors in the structures.

In all the structure-factor calculations, the atomic scattering factors were taken from ref. 11. Tables of observed and calculated structure factors appear in Sup-

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* This assumption necessitates that the molecules possess two-fold symmetry.

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

plementary Publication No. SUP 20384 (7 pp., 1 microfiche).[†]

The fractional co-ordinates of all non-hydrogen atoms and the respective anisotropic thermal parameters are given in Tables 2—4. Table 5 contains bonded distances,

TABLE 2

$Zn(py)_3(NO_3)_2$: (*a*) Atom positions (fractional co-ordinates)

	x/*a*	*y*/*b*	*z*/*c*
Zn	0·5	0·70834(22)	0·25
C(1)	0·3845(10)	0·5829(17)	0·3747(9)
C(2)	0·3532(9)	0·5687(16)	0·4464(9)
C(3)	0·3893(12)	0·6700(18)	0·5133(11)
C(4)	0·4622(13)	0·7720(20)	0·5043(11)
C(5)	0·4339(15)	0·7821(18)	0·4321(9)
C(6)	0·4120(13)	1·0078(16)	0·2540(11)
C(7)	0·4059(11)	1·1530(15)	0·2510(9)
C(8)	0·5	1·2321(22)	0·25
O(1)	0·3779(9)	0·5364(14)	0·1885(8)
O(2)	0·3079(9)	0·7378(12)	0·1572(8)
O(3)	0·2151(8)	0·5523(15)	0·0908(8)
N(1)	0·4524(8)	0·6874(12)	0·3636(6)
N(2)	0·2958(8)	0·6086(13)	0·1421(7)
N(3)	0·5	0·9425(13)	0·25

(*b*) Anisotropic temperature factors (Å²) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Zn(1)	0·039	0·036	0·032	0·000	0·016	0·000
C(1)	0·040	0·063	0·038	−0·011	0·043	0·016
C(2)	0·054	0·075	0·044	−0·032	0·021	0·032
C(3)	0·068	0·099	0·038	−0·022	0·042	−0·016
C(4)	0·101	0·079	0·011	0·004	0·052	0·002
C(5)	0·070	0·053	0·051	0·019	0·041	0·040
C(6)	0·046	0·052	0·044	0·001	0·039	−0·008
C(7)	0·060	0·045	0·082	0·016	0·071	−0·018
C(8)	0·035	0·066	0·023	0·000	0·002	0·000
O(1)	0·066	0·092	0·058	0·002	0·028	0·016
O(2)	0·078	0·048	0·092	−0·022	0·087	−0·015
O(3)	0·044	0·101	0·069	−0·066	−0·007	−0·048
N(1)	0·037	0·063	0·017	−0·013	0·017	−0·004
N(2)	0·029	0·054	0·040	−0·005	0·012	0·006
N(3)	0·025	0·013	0·023	0·000	−0·016	0·000

(*c*) Mean average estimated standard deviations (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Zn	0·002	0·001	0·001	0·002	0·002	0·002
C	0·014	0·011	0·008	0·014	0·017	0·018
O	0·011	0·009	0·008	0·012	0·013	0·014
N	0·010	0·007	0·006	0·010	0·014	0·012

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

TABLE 3

$Co(py)_3(NO_3)_2$: (*a*) Atom positions (fractional co-ordinates)

	x/*a*	*y*/*b*	*z*/*c*
Co	0·5	0·70225(20)	0·25
C(1)	0·3846(9)	0·5846(13)	0·3746(8)
C(2)	0·3515(10)	0·5739(17)	0·4469(9)
C(3)	0·3921(12)	0·6737(17)	0·5132(9)
C(4)	0·4678(13)	0·7764(15)	0·5065(8)
C(5)	0·4931(11)	0·7780(12)	0·4304(8)
C(6)	0·4102(9)	0·9983(12)	0·2549(8)
C(7)	0·4067(11)	0·1443(14)	0·2546(8)
C(8)	0·5	1·2210(15)	0·25
O(1)	0·3859(8)	0·5262(9)	0·1882(5)
O(2)	0·3150(7)	0·7314(9)	0·1616(6)
O(3)	0·2186(7)	0·5502(11)	0·0917(6)
N(1)	0·4513(7)	0·6889(9)	0·3642(5)
N(2)	0·3043(8)	0·5978(11)	0·1450(6)
N(3)	0·5	0·9273(12)	0·25

TABLE 3 (*Continued*)

(*b*) Anisotropic temperature factors (Å²) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Co	0·047	0·039	0·045	0·000	0·040	0·000
C(1)	0·049	0·075	0·066	0·030	0·047	−0·002
C(2)	0·052	0·093	0·075	0·044	0·063	−0·028
C(3)	0·083	0·093	0·065	0·025	0·059	0·005
C(4)	0·098	0·080	0·058	−0·008	0·062	−0·009
C(5)	0·090	0·058	0·058	0·000	0·065	−0·005
C(6)	0·053	0·056	0·068	−0·017	0·036	0·030
C(7)	0·079	0·054	0·077	0·003	0·068	0·019
C(8)	0·083	0·037	0·061	0·000	0·038	0·000
O(1)	0·077	0·070	0·065	0·019	0·032	0·019
O(2)	0·078	0·053	0·092	−0·021	0·068	0·000
O(3)	0·053	0·105	0·090	−0·064	0·037	−0·029
N(1)	0·053	0·055	0·050	−0·005	0·044	−0·010
N(2)	0·048	0·076	0·057	−0·030	0·048	−0·028
N(3)	0·052	0·039	0·058	0·000	0·043	0·000

(*c*) Mean estimated standard deviations (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Co	0·001	0·001	0·001	0·000	0·002	0·000
C	0·007	0·010	0·007	0·013	0·011	0·012
O	0·006	0·006	0·006	0·009	0·009	0·009
N	0·005	0·005	0·005	0·009	0·008	0·008

* See footnote to Table 2.

TABLE 4

$Cu(py)_3(NO_3)_2$: (*a*) Atom positions (fractional co-ordinates

	x/*a*	*y*/*b*	*z*/*c*
Cu	0·5	0·69890(12)	0·25
C(1)	0·3851(7)	0·5925(11)	0·3703(6)
C(2)	0·3856(8)	0·5804(14)	0·4460(7)
C(3)	0·4039(11)	0·6751(14)	0·5153(9)
C(4)	0·4761(12)	0·7749(14)	0·5050(8)
C(5)	0·5042(9)	0·7800(1)	0·4290(6)
C(6)	0·4067(8)	0·9951(9)	0·2496(7)
C(7)	0·4058(8)	1·1504(10)	0·2479(7)
C(8)	0·5	1·2212(15)	0·25
O(1)	0·3804(6)	0·5354(8)	0·1876(5)
O(2)	0·2862(8)	0·7280(10)	0·1458(7)
O(3)	0·2176(7)	0·5187(12)	0·0917(7)
N(1)	0·4569(6)	0·6912(7)	0·3605(5)
N(2)	0·2934(6)	0·5951(10)	0·1397(5)
N(3)	0·5	0·9232(10)	0·25

(*b*) Anisotropic temperature factors (Å²) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	0·051	0·030	0·053	0·000	0·049	0·000
C(1)	0·058	0·059	0·049	−0·024	0·038	−0·043
C(2)	0·064	0·089	0·063	0·004	0·070	−0·041
C(3)	0·078	0·081	0·074	0·023	0·095	0·009
C(4)	0·094	0·061	0·061	−0·002	0·069	0·014
C(5)	0·080	0·044	0·044	−0·009	0·062	−0·015
C(6)	0·062	0·051	0·077	−0·019	0·058	0·012
C(7)	0·072	0·035	0·074	−0·018	0·049	0·009
C(8)	0·070	0·027	0·098	0·000	0·080	0·000
O(1)	0·068	0·059	0·062	−0·008	0·046	0·004
O(2)	0·083	0·046	0·101	−0·024	0·100	−0·041
O(3)	0·059	0·107	0·099	−0·085	0·028	−0·041
N(1)	0·050	0·040	0·053	0·000	0·052	0·003
N(2)	0·041	0·064	0·063	−0·024	0·040	−0·026
N(3)	0·064	0·023	0·055	0·000	0·061	0·000

(*c*) Mean estimated standard deviations (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	0·001	0·001	0·001	0·000	0·001	0·000
C	0·005	0·006	0·005	0·009	0·008	0·009
O	0·004	0·005	0·006	0·008	0·007	0·007
N	0·003	0·004	0·004	0·006	0·006	0·005

* See footnote to Table 2.

[†] 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).

valence angles, intramolecular and intermolecular 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. Details of several molecular planes are given in Table 6.

TABLE 5

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

(*a*) Bonded distances

	Zn	Co	Cu
M–O(1)	2·232(13)	2·207(9)	2·154(7)
M–O(2)	2·418(12)	2·311(9)	2·732(9)
M–N(1)	2·129(10)	2·152(9)	2·018(8)
M–N(3)	2·201(12)	2·124(11)	2·064(9)
N(1)–C(1)	1·35(2)	1·340(15)	1·336(11)
N(1)–C(5)	1·39(2)	1·380(20)	1·350(12)
C(1)–C(2)	1·36(2)	1·331(20)	1·385(13)
C(2)–C(3)	1·41(2)	1·398(21)	1·396(16)
C(3)–C(4)	1·37(2)	1·362(21)	1·348(18)
C(4)–C(5)	1·36(2)	1·403(20)	1·376(15)
N(3)–C(6)	1·32(2)	1·338(13)	1·362(10)
C(6)–C(7)	1·37(2)	1·378(16)	1·428(12)
C(7)–C(8)	1·40(2)	1·403(15)	1·360(12)
N(2)–O(1)	1·26(2)	1·287(13)	1·261(10)
N(2)–O(2)	1·24(2)	1·235(13)	1·248(13)
N(2)–O(3)	1·21(2)	1·223(13)	1·232(12)

(*b*) Interbond angles

	Zn	Co	Cu
O(1)–M–O(2)	53·0(4)	55·8(3)	50·0(3)
O(1)–M–O(1′)	87·2(3)	82·4(3)	91·4(3)
O(1)–M–O(2′)	140·2(3)	137·9(3)	141·3(3)
O(1)–M–N(1)	88·6(3)	91·3(3)	92·0(3)
O(1)–M–N(1′)	83·7(3)	83·7(3)	85·2(2)
O(1)–M–N(3)	136·4(3)	138·8(2)	134·3(2)
O(2)–M–O(2′)	166·8(3)	166·3(3)	168·8(3)
O(2)–M–N(1)	92·4(3)	91·7(4)	92·5(3)
O(2)–M–N(1′)	88·4(4)	89·1(3)	87·9(3)
O(2)–M–N(3)	83·4(3)	83·2(2)	84·4(2)
N(1)–M–N(1′)	169·4(4)	173·3(4)	176·0(3)
N(1)–M–N(3)	95·3(3)	93·4(2)	92·0(2)
C(2)–C(1)–N(1)	124·0(13)	122·9(12)	123·1(9)
C(1)–C(2)–C(3)	119·3(15)	118·5(13)	118·4(10)
C(2)–C(3)–C(4)	116·9(15)	119·9(14)	118·4(10)
C(3)–C(4)–C(5)	122·5(16)	117·1(13)	120·8(11)
C(4)–C(5)–N(1)	120·5(15)	124·3(12)	121·8(10)
M–N(1)–C(1)	123·4(9)	121·6(8)	121·0(6)
M–N(1)–C(5)	119·9(9)	121·1(8)	121·3(6)
C(1)–N(1)–C(5)	116·7(12)	117·1(10)	117·6(8)
C(7)–C(6)–N(3)	120·9(13)	121·8(11)	119·1(8)
C(6)–C(7)–C(8)	119·3(14)	119·3(12)	118·5(10)
C(7)–C(8)–C(7′)	116·4(14)	117·9(12)	122·7(11)
M–N(3)–C(6)	118·5(8)	120·0(6)	119·1(5)
C(6)–N(3)–C(6′)	123·0(13)	120·0(11)	121·9(11)
M–O(1)–N(2)	101·0(9)	98·0(7)	109·9(6)
M–O(2)–N(2)	92·6(8)	91·6(6)	82·3(6)
O(1)–N(2)–O(2)	112·6(11)	114·0(9)	117·2(8)
O(1)–N(2)–O(3)	121·4(14)	121·0(10)	119·7(9)
O(2)–N(2)–O(3)	126·0(12)	125·0(11)	123·0(9)

(*c*) Intramolecular contacts $<3{\cdot}5$ Å

	Zn	Co	Cu
M ··· C(1)	3·09	3·07	2·94
M ··· C(5)	3·07	3·06	2·95
M ··· C(6)	3·03	3·02	2·97
M ··· N(2)	2·77	2·68	2·84
O(1) ··· C(1)	3·49	3·42	3·45
O(1) ··· C(1′)	3·03	3·10	2·96
O(1) ··· O(1′)	3·08	2·91	3·08
O(1) ··· O(2)	2·08	2·12	2·13
O(1) ··· O(3)	2·16	2·18	2·17
O(1) ··· N(1)	2·91	2·91	2·83
O(1) ··· N(1′)	3·05	3·12	3·00
O(2) ··· C(5)	3·30	3·27	3·29
O(2) ··· C(6′)	3·05	2·98	3·09
O(2) ··· O(3)	2·18	2·18	2·18
O(2) ··· N(1)	3·18	3·13	3·33
O(2) ··· N(1′)	3·29	3·20	3·47
O(2) ··· N(3)	3·08	2·95	3·26

TABLE 5 (*Continued*)

(*d*) Intermolecular contacts $<3{\cdot}65$ Å

	Zn	Co	Cu
O(1) ··· C(3^{I})	3·49	3·45	3·47
O(1) ··· C(8^{II})	3·25	3·23	3·28
O(2) ··· C(7^{III})	3·57	3·59	3·48
O(3) ··· C(2^{I})	3·53	3·52	3·47
O(3) ··· C(3^{I})	3·55	3·57	3·49
O(3) ··· C(4^{IV})	3·46	3·44	3·34
O(3) ··· C(4^{III})	3·48	3·48	3·52
O(3) ··· C(5^{IV})	3·49	3·55	3·52
O(3) ··· C(5^{III})	3·59	3·63	3·63
O(3) ··· C(6^{III})	3·43	3·44	3·41
O(3) ··· C(7^{IV})	3·52	3·49	3·63
N(2) ··· C(7^{III})	3·54	3·58	3·59

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

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

TABLE 6

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)				
(i) Zn	0·4344	0·0901	−0·8962	1·0476
[O(1) −0·003, O(2) −0·003, O(3) −0·003, N(2) 0·009, Zn 0·325]				
(ii) Co	0·4115	0·1149	−0·9041	1·1419
[O(1) −0·002, O(2) −0·002, O(3) −0·002, N(2) 0·006, Co 0·267]				
(iii) Cu	0·3992	0·1077	−0·9105	1·0288
[O(1) −0·005, O(2) −0·005, O(3) −0·005, N(2) 0·014, Cu 0·263]				
Plane (2): C(1)—(5), N(1)				
(i) Zn	−0·7875	0·5890	−0·1816	−1·2019
[C(1) −0·003, C(2) −0·022, C(3) 0·029, C(4) −0·010, C(5) −0·015, N(1) 0·022, Zn 0·062]				
(ii) Co	−0·7827	0·5965	−0·1777	−1·0632
[C(1) −0·018, C(2) −0·006, C(3) 0·018, C(4) −0·006, C(5) −0·018, N(1) 0·030, Co 0·020]				
(iii) Cu	−0·7429	0·6533	−0·1461	−0·5517
[C(1) −0·001, C(2) −0·002, C(3) −0·003, C(4) 0·013, C(5) −0·016, N(1) 0·010, Cu 0·047]				
Plane (3): C(6)—(8), N(3)				
(i) Zn	−0·3536	−0·0071	−0·9354	−4·0768
[C(6) −0·020, C(7) 0·019, C(8) −0·009, N(3) 0·010, Zn 0·026]				
(ii) Co	−0·3910	−0·0010	−0·9204	−4·1552
[C(6) −0·003, C(7) 0·003, C(8) −0·001, N(3) 0·002, Co 0·004]				
(iii) Cu	−0·2995	−0·0041	−0·9541	−3·7670
[C(6) −0·011, C(7) 0·011, C(8) 0·006, N(3) −0·006, Cu 0·014]				

Dihedral angles (°) between planes

	Zn	Co	Cu
(1)–(2)	82·8	84·7	84·7
(1)–(3)	46·8	47·8	41·5
(2)–(3)	63·6	62·0	68·9

The atomic numbering scheme for the complexes is shown in Figure 1 and Figure 2 shows the packing arrangement in the unit cell.

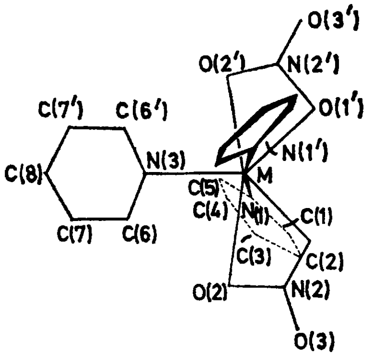

FIGURE 1 A view of the Gonnon molecular arrangement along *c* showing the atomic numbering

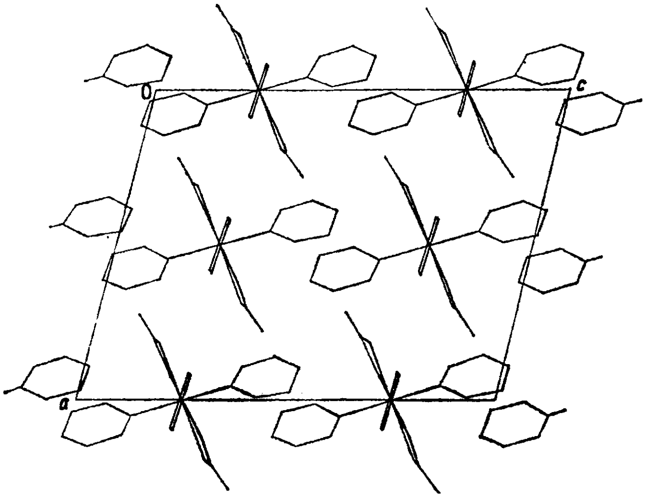

FIGURE 2 The molecular packing viewed along the *b* axis

DISCUSSION

Our three analyses reveal that the complexes possess monomeric structures in which all the pyridine and nitrate groups are co-ordinated to the central metal atom in accordance with the predictions on the i.r. and conductivity measurements.[1-5] However, the crystallographic requirement that the molecules possess two-fold symmetry [the metal atom and atoms N(3) and C(8) of one of the pyridine moieties lie on the symmetry axis] (Figure 1), precludes those predicted structures [1,4,5] which possessed non-equivalent nitrato-co-ordination.

The overall molecular geometries of the three complexes show slight but marked differences, particularly in the detailed nitrato-co-ordination. In all three cases, the nitrate groups are asymmetrically orientated to the metal atom with the degree of asymmetry increasing in the order $Co^{II} < Zn^{II} \ll Cu^{II}$. For the cobalt and zinc complexes, the bonding is unequivocally bidentate whereas, for the copper complex the asymmetry of the copper–nitrate co-ordination is so great that the nitrato-groups are on the borderline between bi- and uni-dentate co-ordination.

The shortest metal–ligand distances in the cobalt and zinc complexes are significantly longer than those found in corresponding Co^{II} and Zn^{II} four-, five-, and six-co-ordinate complexes.[12] This lengthening of bond lengths by *ca.* 0·1 Å has also been found for the $M(NO_3)_4^{2+}$ ion ($M = Co^{II}$, Mn^{II}, and Zn^{II}).[13,14] In this latter series of complexes, the asymmetric bidentate co-ordination of the nitrate groups apparently provides the most favourable steric arrangement of four nitrate moieties around a small central metal ion to produce eight-co-ordinate species. Since the steric requirements of seven-co-ordination complexes cannot be much less, particularly when three positions are occupied by bulky pyridine groups, the asymmetry of the nitrato-co-ordination and lengthening of other metal–ligand bonds is not unexpected. For $Cu(py)_3(NO_3)_2$, the nitrate groups are much more asymmetric, an arrangement which relieves the steric requirements at the copper atom and enables the pyridine functions to be relatively more closely bound.

The difference in M–O distances is significant [M–O(2) –M–O(1) is 0·104 Å (Co), 0·186 Å (Zn), and 0·560 Å (Cu)] and the trend in individual metal–oxygen bond lengths is reflected in those frequencies assigned to ν(M–O) in the far i.r.[1-3] For the cobalt and zinc complexes the bond lengths are in Irving–Williams order but for the copper compound the situation is apparently more complicated than the series would predict.

For the cobalt and zinc complexes, the formal arrangement around the metal atom is seven-co-ordinate in a structure which may be related to a five-co-ordinate square-based pyramidal geometry using the line of centre approach of Cotton *et al.*,[14] where the nitrate groups are considered to occupy single co-ordination sites. Yet another interpretation of the stereochemistry may be achieved by considering the completion of a distorted octahedral co-ordination using as the sixth donor position, a line bisecting the M–O(1) and M–O(1′) bonds. This approach becomes relatively more important when the distortion of the copper complex is considered, and has already been invoked in descriptions of the molecular geometries of the other copper complexes, $[Cu(py)_2(NO_3)_2]_2,py$,[15] $Cu(\alpha\text{-picoline})_2(NO_3)_2$,[16] and $Cu(NO_3)_2,2{\cdot}5H_2O$.[17] In these last-named complexes, the copper atom is surrounded by four short-bonded atoms in a square-planar arrangement. Below the plane are the two longer-bonded atoms of the nitrate groups and above is an atom in a long-bond position although, for $Cu(\alpha\text{-picoline})_2(NO_3)_2$, this

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latter position is blocked by the *cis*-α-methyl groups. In the present copper complex, the pyridine groups occupy three corners of a square plane whilst the fourth corner extends midway between the two shortest-bonded oxygens. Occupying the axial positions to this plane are the long-bonded oxygens of the nitrato-groups, so that effectively, by comparison with the cobalt and zinc complexes, a distortion of the type predicted by the Jahn–Teller effect is observed. The formal ionic radius of Cu^{II} falls between those of Co^{II} and Zn^{II} and, moreover, the individual steric bulk of each ligand does not alter from complex to complex throughout this series. Since all three complexes adopt the same crystal packing, the molecular geometry of $Cu(py)_3(NO_3)_2$ might be expected to be intermediate between those for Co^{II} and Zn^{II}. Since this is not so, the sole remaining factor to be accounted for is the nature of the bonding in the copper complex compared to that in the other two. The Jahn–Teller effect [18] predicts just such a static distortion as we have observed and the series of complexes may thus be taken as a satisfactory demonstration of the existence of the effect.

For the cobalt complex, a slight polarisation effect is observed in the nitrate groups, with the N–O bond adjacent to the strongest metal–oxygen interaction [N–O(1)] longer than the terminal N–O bond [N–O(3)]. In the corresponding bonds for the zinc and copper complexes, the same trend is observed although, in these cases, the differences are not statistically significant. The O–N–O angles all show distortions from the trigonal value of 120°, such that the largest angle is opposite the strongest M–O interaction in each case. The degree of bidentate character of the nitrate groups is reflected in the M–O(1)–N(2) angles [M–O(1)–N(2) 98·0(7) (Co), 101·0(9) (Zn), and 109·9(6)° (Cu)] which in the copper complex approach the angle expected for unidentate co-ordination of 110°.[19]

In the molecular structures, all the groups are arranged so as to minimise steric interaction. Intermolecular contacts are all equal to or greater than the sums of the relevant van der Waals' radii.

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

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