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# The Crystal Structure of Ammonium Tris[4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione]-cadmium(II)

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*The crystal structure of ammonium tris[4,4,4-trifluoro-1-(2-furyl)1,3-butanedione]cadmium(II),* $NH_4[Cd(C_8H_4O_3F_3)_3]$, *has been determined using 655 visually estimated reflection intensities. Full matrix least squares refinement led to* $R = 0.086$ *and* $Rw = 0.070$. *The space group is* $R\bar{3}$ *and there are six molecules in the triply primitive hexagonal cell which has* $a = 18.46(3)$ *and* $c = 14.68(2)$ Å. *The structure consists of discrete* $NH_4^+$ *cations, and anions containing hexacoordinated cadmium with the three bidentate ligands related by a crystallographic three-fold axis. The geometry of the coordination sphere is distorted 30–40% from the expected octahedron towards a trigonal prism. This distortion appears to be due to the proximity of the small cation to the coordinating ligand oxygen atoms. X-ray powder patterns of the corresponding chelates of the divalent metals Mn, Fe, Co, Ni and Zn indicate that these compounds are isostructural with the Cd chelate.*

## Introduction

X-ray structural studies of β-diketone chelates with trivalent lanthanides carried out in these laboratories have shown 8-fold coordination of the metal in all cases. Two types of compound were formed, the neutral tri chelates where coordination is completed by water molecules [1] and the tetrakis chelate anions, with ammonium or tetrabutylammonium as a cation [2, 3]. In the present paper an extension of this work to similar chelates with metals of the transition series is reported.

The crystal structure of tetrabutylammonium tris(acetylacetonato)cobalt(II) had been studied earlier [4], and found to have octahedral coordination of the metal. However, in this compound the bulky cation could not approach closely to the coordination sphere and we have therefore used the small ammonium ion to study its effect on the coordination geometry. Using 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione (HFTA) as a ligand compounds of the divalent transition metals Mn, Fe, Co, Ni, Zn and Cd were made in which three ligands combined with one metal atom and $NH_4^+$ was the compensating cation [5]. Of these the Cd compound was selected for single crystal structure determination while investigation of the others was largely confined to the powder patterns.

## Experimental

### *Preparation*

HFTA was produced by the Claisen condensation of ethyltrifluoroacetate and 2-furylmethylketone [5] and the ammonium salt prepared directly from the

TABLE I. Summary of Analytical Data.

| Formula | % Metal | | %C | | %H | | %N | |
|---|---|---|---|---|---|---|---|---|
| | calc. | found | calc. | found | calcd. | found | calcd. | found |
| $NH_4Mn(FTA)_3$ | 7.98 | 8.02 | 41.88 | 42.04 | 2.34 | 2.46 | 2.04 | 1.99 |
| $NH_4Fe(FTA)_3$ | 8.10 | 8.20 | 41.82 | 41.97 | 2.34 | 2.48 | 2.03 | 2.07 |
| $NH_4Co(FTA)_3$ | 8.51 | 7.58 | 41.63 | 41.57 | 2.33 | 2.46 | 2.02 | 2.00 |
| $NH_4Ni(FTA)_3$ | 8.48 | 8.03 | 41.65 | 41.70 | 2.33 | 2.44 | 2.02 | 1.89 |
| $NH_4Zn(FTA)_3$ | 9.36 | 9.05 | 41.25 | 41.36 | 2.31 | 2.44 | 2.01 | 2.03 |
| $NH_4Cd(FTA)_3$ | 15.07 | 15.45 | 38.65 | 39.06 | 2.16 | 2.24 | 1.88 | 2.12 |

TABLE II. Crystallographic Data for $NH_4Cd(FTA)_3$.

| | |
|---|---|
| M.W. = 745.8 | |
| Crystallographic System: | Rhombohedral |
| Space Group: | $R\bar{3}$ |
| Unit Cell Parameters: | $a = 18.46(3)$ A[a] |
| (Triply Primitive | $c = 14.68(2)$ A |
| Hexagonal Cell) | $V = 4332$ A$^3$ |
| | $Z = 6$ |
| $d_{calc}$ = 1.72 g/cm$^3$ | $\lambda_{MoK\alpha}$ = 0.7107 A |
| $d_{obs}$ = 1.73 g/cm$^3$ | $\mu_{MoK\alpha}$ = 4.96 cm$^{-1}$ |
| $F_{000}$ = 2,206 | |

[a] Here and throughout this paper the estimated standard deviations, shown in parentheses, are right adjusted to the least significant digit in the preceding number.

reaction mixture. The metal chelates were prepared by mixing separate solutions in 95% ethanol of the metal chloride or nitrate and 4 mol of $NH_4FTA$ (1 mol excess) per mole of the metal salt. Crystals, where these were obtained, were grown by slow evaporation. Analytical data are given in Table I.

*X-ray*

An approximately cylindrical crystal of $NH_4Cd(FTA)_3$, measuring 0.3 mm in length and 0.2 mm in diameter was selected, and the crystal data are given in Table II. The cell dimensions were measured using Al and Ag wires as standards. The density was determined by flotation at 25 °C in $CCl_4$–$CHBr_3$ solution. Intensity data were collected for the reciprocal lattice levels *h0l–h5l* with Zr-filtered MoKα radiation using the precession technique. For each level four or five films were taken with timed exposures running from 2–48 hours. Intensities were estimated visually by comparison with a time calibrated standard scale. The different levels were correlated by means of symmetry related reflections and a set of $F_o$s derived by application of Lorentz-polarization corrections. Individual standard deviations were estimated for the intensity measurements, and these were carried through all stages of the data reduction to give proper values of $\sigma_F$. Although the linear absorption coefficient is low (4.96 cm$^{-1}$) absorption corrections were calculated for twelve reflections distributed through reciprocal space. Since the differences were negligible absorption corrections were not applied. The total number of observed reflections was 655.

For the other five transition metal chelates and also the Cd compound, powder patterns were taken on a Philips powder diffractometer using Ni-filtered CuKα radiation. For the Mn and Zn compounds twinned crystals were obtained, and photographs of these showed similar cell dimensions to those of $NH_4Cd(FTA)_3$.

*Structure Determination and Refinement*

The Patterson function for $NH_4Cd(FTA)_3$ showed a dominant peak at 0, 0, ½. Accordingly, the Cd atoms were placed in the 6(c) positions, ±, 0, 0, *z*, of the space group $R\bar{3}$, with $z = ¼$. This required that the $NH_4^+$ ions lie at the centrosymmetric 3(a), 3(b) positions, 0, 0, 0 and 0, 0, ½, with the H atoms disordered. One ligand would then complete the asymmetric unit with the atoms in the general 18(f) positions, the other two ligands being generated by the three-fold axis. All C, N, O and F atoms were found from electron density maps based initially on the phase angles calculated from the Cd positions, and the space group assignment seems justified by refinement.

Full matrix least squares refinement of all the free positional and anisotropic thermal parameters for the non-hydrogen atoms was carried out and gave Rw = 0.072. A difference electron density map did not show the hydrogen atoms, but did indicate some disorder in the $CF_3$ group, notably a splitting of F(3). Final refinement was carried out using the scattering factor for a disordered $NH_4^+$ ion [6, 7] and gave R = 0.086, Rw = 0.070. The other scattering factors used were those of Hanson *et al.* [8] with the anomalous scattering correction for Cd taken from the International Tables [9]. The function minimized in refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma_F^2$, σ being obtained as described above. The unobserved reflections were treated by the method of High and Kraut [10]. A table of observed and calculated structure factors may be obtained from the Editor. Major computing programs used in the structure analysis are FORDAP [11], ORFLS [12], ORFFE [13].

Since the powder patterns of all six transition metal chelates were very similar, it was possible to determine the cell constants of all the chelates, as follows. From the structural parameters for $NH_4Cd(FTA)_3$ a powder pattern was computed, and by comparison with the observed pattern fourteen of the strongest maxima were indexed. The raw 2θ values from the powder pattern of the Cd chelate differed slightly from those calculated from the cell dimensions derived from single crystal measurements. An empirical factor of 1.005 was found to give the best agreement, and this was applied to the raw 2θ values for the other compounds. Eight to ten of the strongest maxima in the powder patterns of the other chelates were indexed by comparison with the Cd chelate. Due to the relative simplicity of the equation for interplanar spacing in the hexagonal system, it can be rearranged to a linear form in which $(a^*)^2$ is the intercept, $(c^*)^2$ is the slope, $l^2/(h^2 + hk + k^2)$ is the independent variable and the reciprocal of $d^2(h^2 + hk + k^2)$ is the dependent variable. Cell

TABLE III. Cell Dimensions Obtained from Powder Patterns of Chelates Formed by Metals of the First Transition Series.

| *Metal* | *a* (A) | *c* (A) |
|---|---|---|
| Mn | 18.37 (2) | 14.53 (1) |
| Fe | 18.38 (3) | 14.28 (1) |
| Co | 18.30 (4) | 14.44 (2) |
| Ni | 18.23 (4) | 14.31 (2) |
| Zn | 18.21 (6) | 14.50 (3) |

dimensions were obtained by a direct least squares fit [14] and the proper e.s.d.s of *a* and *c* derived [15]. The results were checked with a reiterative trial and error fitting program, CFT3 [16], using the more usual form of the equation for interplanar spacing [20]. The two sets of cell dimensions were close, with correlation coefficients of 0.944 for *a* and 0.933 for *c*, and only the results of the first method are shown in Table III.

To provide stronger evidence that all the chelates are isostructural the powder patterns were calculated by substituting the appropriate metal form factor for that of Cd. Agreement between the calculated and observed patters was good in all cases, but not as good as for the Cd chelate. This indicates that while the whole series is probably isostructural, minor changes in parameters occur between different members.

## Results and Discussion

The refined positional parameters are given in Table IV and the anisotropic thermal parameters in Table V. The inter- and intramolecular dimensions are shown in Fig. 1. Estimated standard deviations for the bond distances are 0.01 Å for Cd–O bonds, 0.02 Å for C–O, 0.02–0.04 Å for C–C and 0.03–0.05 Å for C–F. The e.s.d. s for bond angles range from 0.5° for O(1)–Cd–O(2) to 2–4° for F–C–F angles. The C–F distances were corrected by the riding model [17] and the corrected distances are more uniform. However, since disorder probably exists in the $CF_3$ group, all e.s.d s involving F atoms must be regarded as low.

TABLE IV. Fractional Atomic Coordinates.

| *Atom* | *x* | *y* | *z* |
|---|---|---|---|
| Cd | 0.0(0) | 0.0(0) | 0.24987(11) |
| N(1) | 0.0(0) | 0.0(0) | 0.0(0) |
| N(2) | 0.0(0) | 0.0(0) | 0.5(0) |
| F(1) | 0.1934(8) | 0.1584(10) | 0.0165(7) |
| F(2) | 0.2647(11) | 0.1295(15) | 0.0847(10) |
| F(3) | 0.2763(16) | 0.2513(11) | 0.0867(13) |
| O(1) | 0.1081(10) | 0.0707(9) | 0.1587(6) |
| O(2) | 0.0795(8) | 0.1086(8) | 0.3424(6) |
| O(3) | 0.1338(9) | 0.2125(11) | 0.4819(10) |
| C(1) | 0.2437(28) | 0.1861(20) | 0.0957(17) |
| C(2) | 0.1727(14) | 0.1423(18) | 0.1706(10) |
| C(3) | 0.1911(11) | 0.1944(11) | 0.2470(11) |
| C(4) | 0.1449(14) | 0.1738(13) | 0.3294(11) |
| C(5) | 0.1777(15) | 0.2387(17) | 0.4007(12) |
| C(6) | 0.2434(14) | 0.3151(16) | 0.4009(13) |
| C(7) | 0.2381(18) | 0.3406(21) | 0.4974(25) |
| C(8) | 0.1728(20) | 0.2820(24) | 0.5390(20) |

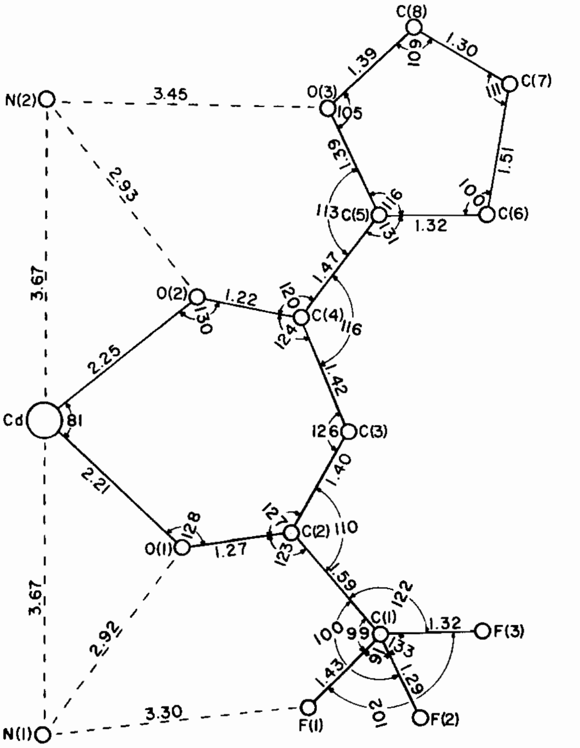

Fig. 1. Bond distances, bond angles and short cation–anion contacts in $NH_4Cd(FTA)_3$.

The crystal structure consists of $NH_4^+$ and $Cd(FTA)_3^-$ ions arranged alternately along the three-fold axis. The stereochemistry of the coordination sphere is shown in Fig. 2. The geometry is considerably distorted from an octahedron towards a trigonal prism. The relative rotation of the two parallel equilateral triangles of oxygen atoms, perpendicular to *c*, is 35°. This angle would be 60° for an octahedron and 0° for a trigonal prism. This distortion can also be described by the method of Muetterties and Guggenberger [18]. The dihedral angles between adjacent faces of a regular octahedron are 70.5°. For a trigonal prism these angles divide into three groups, 0°, 120° and 90°. The average measured values are 46°, 91° and 75° respectively, indicating about 30% trigonal prismatic character, as compared to the

TABLE V. Anisotropic Thermal Parameters. The temperature factors used were of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cd | 0.00854(10) | 0.00854(10) | 0.00327(6) | 0.00427(5) | 0.0(0) | 0.0(0) |
| N(1) | 0.0143(17) | 0.0143(17) | 0.0040(14) | 0.0072(8) | 0.0(0) | 0.0(0) |
| N(2) | 0.0186(20) | 0.0186(20) | 0.0031(13) | 0.0093(10) | 0.0(0) | 0.0(0) |
| F(1) | 0.0131(9) | 0.0222(13) | 0.0095(7) | 0.0071(10) | 0.0050(6) | 0.0057(8) |
| F(2) | 0.0160(11) | 0.0222(20) | 0.0129(10) | 0.0060(13) | 0.0022(9) | −0.0021(12) |
| F(3) | 0.0300(21) | 0.0112(12) | 0.0228(16) | −0.0103(15) | 0.0178(15) | −0.0023(12) |
| O(1) | 0.0109(10) | 0.0124(10) | 0.0054(6) | 0.0060(9) | 0.0027(7) | 0.0012(6) |
| O(2) | 0.0091(8) | 0.0077(8) | 0.0056(5) | 0.0019(7) | −0.0006(5) | −0.0007(6) |
| O(3) | 0.0127(11) | 0.0153(13) | 0.0107(8) | 0.0059(10) | −0.0011(8) | −0.0051(9) |
| C(1) | 0.0241(39) | 0.0093(20) | 0.0082(12) | 0.0070(23) | 0.0035(18) | −0.0011(14) |
| C(2) | 0.0091(15) | 0.0148(20) | 0.0042(7) | 0.0024(13) | 0.0013(9) | 0.0004(11) |
| C(3) | 0.0105(13) | 0.0103(13) | 0.0085(9) | 0.0066(11) | 0.0003(10) | 0.0002(10) |
| C(4) | 0.0088(14) | 0.0067(12) | 0.0081(10) | 0.0047(11) | −0.0010(11) | −0.0005(10) |
| C(5) | 0.0071(12) | 0.0130(17) | 0.0091(11) | 0.0042(13) | −0.0024(10) | −0.0057(12) |
| C(6) | 0.0072(13) | 0.0112(13) | 0.0139(15) | 0.0038(13) | −0.0037(11) | −0.0063(13) |
| C(7) | 0.0091(18) | 0.0154(27) | 0.0214(30) | 0.0056(18) | −0.0054(19) | −0.0094(21) |
| C(8) | 0.0104(21) | 0.0170(29) | 0.0187(24) | 0.0070(20) | −0.0046(19) | −0.0087(23) |

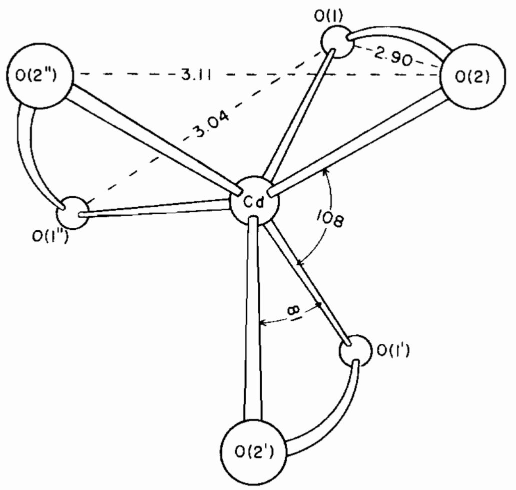

Fig. 2. The geometry of the Cd coordination sphere in $NH_4Cd(FTA)_3$.

twist angle measurement which could be interpreted as about 40% distortion towards a trigonal prism.

It seems probable that this distortion towards trigonal prismatic geometry is caused by the proximity of the small cations to the chelating oxygen atoms. The distances N(1)–O(1) and N(2)–O(2) are 2.92 and 2.93 Å respectively (Fig.2), in the range of hydrogen bonded distances. In the analogous $Cd(TTA)_3^-$* anion, with tetrabutylammonium as the cation, this situation cannot be realized and the anion geometry is octahedral [19].

TABLE VI. Least Squares Mean Plane for the Six-Membered Ring Formed by the Cd Atom and the Ligand Backbone, and Distances of Individual Atoms from the Plane.

*Plane*: $-0.812\,X + 0.451\,Y - 0.371\,Z + 1.408 = 0$

| *Atom* | *Distance* (Å) |
|---|---|
| Cd | 0.05(1) |
| O(1) | −0.04(2) |
| C(2) | −0.02(3) |
| C(3) | 0.06(2) |
| C(4) | −0.00(3) |
| O(2) | −0.05(2) |

The least squares mean plane for the six-membered ring of the Cd atom and the ligand backbone is given in Table VI. The deviations from planarity are due to a buckling of 6° about the line O(1)–O(2). The 5 ligand atoms are coplanar within experimental error, and their plane makes an angle of 5° with the furyl ring.

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