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SYNTHESIS, CHEMICAL PROPERTIES AND X-RAY STRUCTURE OF THE BIS-ACETONE ADDUCT $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ (TPyEA = TRIS(1-PYRAZOLYLETHYL)AMINE)

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Summary

The bis-acetone adduct $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ has been prepared and characterized in the solid state. The structure of the compound has been determined by single-crystal X-ray techniques (space group $P\bar{1}$; a 20.159(10), b 13.200(7), c 13.359(8) Å; α 117.77(8), β 102.53(9), γ 91.81(8)°; $Z = 2$). The cobalt atom is six-coordinated by the four nitrogen atoms of the TPyEA ligand and by the two oxygens of the acetone molecules. The complex undergoes transformations, mainly involving the acetone molecules, in the solid state and the possible products of these transformations are discussed. The complex $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ when dissolved in acetone catalyses the formation of diacetone alcohol and, in lower yield, of mesityl oxide.

Introduction

Only a few transition metal complexes containing acetone as a ligand have been investigated [1]. Most acetone complexes are unstable, and cannot be isolated in the solid state. The instability increases with the number of coordinated acetone molecules, so that the tris-acetone complexes are thought to exist only in acetone solution, where the solvated molecules can be easily replaced by a number of σ and π donors [2–4].

We have found that cobalt(II) and nickel(II) and the ligand tris(1-pyrazolylethyl)amine (TPyEA) form bis-solvent adducts $[M(solvent)_2(TPyEA)](BPh_4)_2$ (solvent = CH_3CN, $(CH_3)_2CO$) which can be isolated in the solid state, and we now describe the synthesis, some chemical properties, and the structure determination of the bis-acetone adduct of cobalt(II) $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$.

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TABLE 1

SELECTED BOND LENGTHS (Å) AND ANGLES (°) IN THE STRUCTURE OF $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ [a]

Co-O(1)	2.226(5)	O(1)-C(16)	1.21(1)
Co-O(2)	2.351(8)	C(16)-C(17)	1.55(2)
Co-N(1)	2.195(6)	C(16)-C(18)	1.57(2)
Co-N(2)	2.048(9)	O(2)-C(19)	1.19(1)
Co-N(3)	2.059(7)	C(19)-C(20)	1.45(3)
Co-N(4)	2.037(9)	C(19)-C(21)	1.54(2)
O(1)-Co-O(2)	85.1(3)	N(1)-Co-N(4)	94.8(3)
O(1)-Co-N(1)	175.3(3)	N(2)-Co-N(3)	96.9(3)
O(1)-Co-N(2)	85.7(3)	N(2)-Co-N(4)	166.5(3)
O(1)-Co-N(3)	88.0(3)	N(3)-Co-N(4)	95.2(3)
O(1)-Co-N(4)	88.7(3)	O(1)-C(16)-C(17)	120(1)
O(2)-Co-N(1)	92.2(3)	O(1)-C(16)-C(18)	121(1)
O(2)-Co-N(2)	84.3(3)	C(17)-C(16)-C(18)	119(1)
O(2)-Co-N(3)	172.9(3)	O(2)-C(19)-C(20)	122(1)
O(2)-Co-N(4)	83.0(3)	O(2)-C(19)-C(21)	118(1)
N(1)-Co-N(2)	90.1(3)	C(20)-C(19)-C(21)	120(1)
N(1)-Co-N(3)	94.8(3)		

[a] Atoms O(1), C(16)-C(18) and O(2), C(19)-C(21) belong to the two acetone molecules.

Results and discussion

Crystal structure of $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$

The title compound is high spin ($\mu_{eff} = 4.52$ μB). Its electronic spectrum with bands at 7400, 9300, 18,200 and 21,000 cm^{-1} is suggestive of a six-coordinate structure. The infrared spectrum of a freshly prepared sample shows a strong band at 1700 cm^{-1} with a shoulder at 1690 cm^{-1} (Fig. 1 (a)) attributable to C=O stretching of the acetone molecules. However, these frequencies are only slightly lower than that of the free acetone molecule (1710 cm^{-1}) and do not, in themselves, confirm the coordination of both acetone molecules. Consequently, we decided to determine the crystal structure of the bis-acetone complex in order to determine the mode of coordination of the acetone molecules and to extend the scarce information on the chemistry of acetone as coligand.

The structure consists of $[Co(Me_2CO)_2(TPyEA)]^{2+}$ cations and BPh_4^- anions. The metal atom is six-coordinated, with approximate octahedral geometry, by the four nitrogen donor atoms of the TPyEA ligand and by the oxygen atoms of the two acetone molecules, lying in *cis* position with respect to each other.

A view of the cation is shown in Fig. 2. Selected values of bond distances and angles are listed in Table 1. All Co-N distances are shorter (by 0.05 Å in the mean) than those found in the $[CoBr(TPyEA)]_2^{2+}$ dinuclear cation [5], where the TPyEA ligand spans two adjacent faces of an octahedron about each metal center, as in the present mononuclear complex. The two Co-O bond lengths (Co-O(1) 2.226(5), Co-O(2) 2.351(8) Å) are considerably different from each other, the longer one being formed by the acetone molecule lying approximately in the plane of the peripheral *N* donors of the TPyEA ligand. Such structural feature may provide a rationalization for the reversible transformation which the compound undergoes in the solid state when it is heated for few minutes at temperatures below 100°C (a change in colour from deep red to magenta is observed upon heating and a change from six to five in the coordination number is indicated by the electronic spectrum). Actually a five-coordinate structure could be reached with a modest conformational rearrangement by further elongation of the long Co–O(2) bond, accompanied by a decrease of the N(2)–Co–N(4) angle (Fig. 2). Reversible transformations in the solid state involving a change in coordination number are not uncommon for the complexes formed by the TPyEA ligand [5].

Values of bond distances and angles within the acetone molecules (Table 1) essentially agree with those of the uncoordinated molecule [6]. The apparent shortening of the C(19)–C(20) bond (1.45(3) Å), is probably due to uncorrected effects of thermal motion.

Thermal and chemical behaviour of the complex $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ *(I)*

The bis-acetone complex is stable only in a dry atmosphere at room temperature, otherwise it slowly undergoes irreversible transformations mainly involving the acetone molecules. These transformations have been followed by infrared and visible spectroscopy and (in part) by mass spectrometry.

When the six-coordinated deep red complex I is heated under vacuum at a temperature of ca. 65°C for 24 h (a), or is allowed to stand at room temperature in a water-saturated atmosphere for 12 h (b), it is transformed to magenta compounds (compound II (a) or III (b)) which contain high-spin five-coordinated cobalt(II) as indicated by their reflectance spectra, which are identical with each other, with bands at 5900, 14,500, 18,500 and 20,800 cm^{-1} [5,7]. The above transformations affect the elemental analyses very little (see Experimental) eventhough the acetone molecules are not longer present in the material, as shown by the infrared and mass spectra. In particular, the $\nu(CO)$ of acetone at 1700 cm^{-1} is replaced in the infrared spectrum of compund II by a strong band at 1620 cm^{-1} (Fig. 1(b)). Moreover, a new band is found at 3500 cm^{-1}. In the spectrum of compound III two new bands are present at 1607 and 1620 cm^{-1} (Fig. 1(c)) in addition to that at 3500 cm^{-1}. Mass spectra have been determined for compounds I, II and III. The mass spectrum of compound I up to 200°C shows only peaks typical of the acetone molecule, suggesting that this molecule is released intact by the solid compound in these conditions. On the other hand, the spectra of compounds II and III under the same experimental conditions do not show any peak assignable to the acetone molecule.

The results suggest that as a consequence of heating or exposure to the moisture the two acetone molecules in complex I react to produce a new species, which may be an alcohol molecule with unsaturated carbon–carbon bonds (IR bands at 3500 and near 1620 cm^{-1}) which behaves as a unidentate ligand (five-coordination of cobalt(II) inferred from the electronic spectra).

In order to tackle this problem a saturated solution of compound I in acetone was refluxed for several hours ($\leqslant$ 24 h). The organic products in the resulting solution were identified by means of gas chromatography as acetone, diacetone alcohol (4-hydroxy-4-methylpentan-2-one), and mesityl oxide (4-methyl-3-penten-2-one). The amounts of the last two products varied from run to run with average values of 10% diacetone alcohol and 2% mesityl oxide. This is in keeping with previous reports that mesityl oxide and diacetone alcohol can be formed by aldol condensation of acetone molecules under catalysis by ruthenium tris-acetone adducts in acetone solution [2], as well as by cobalt and molybdenum complexes in the same solvent [8]. In one case

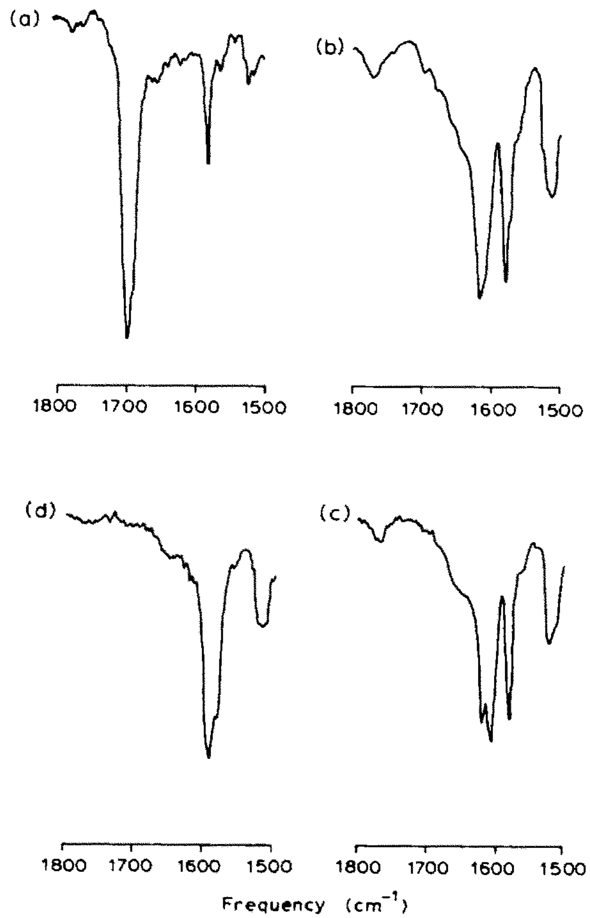


Fig. 1. Infrared spectra in the 1500–1800 region of: (a) [Co(Me$_2$CO)$_2$(TPyEA)] (BPh$_4$)$_2$; (b) complex II obtained by heating; (c) complex III obtained in a water-saturated atmosphere; (d) complex IV obtained from mesityl oxide solution.

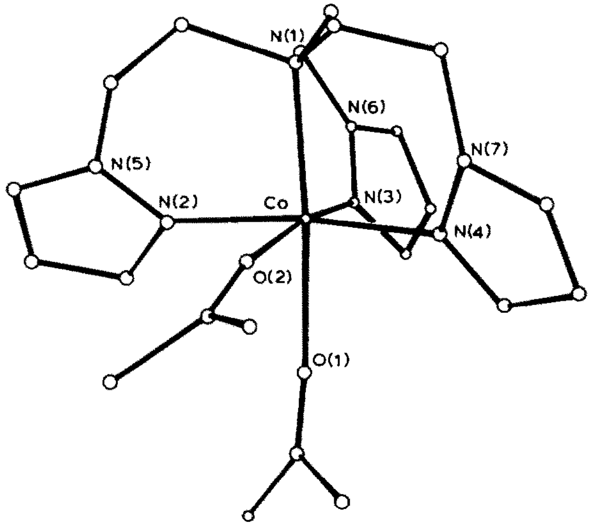


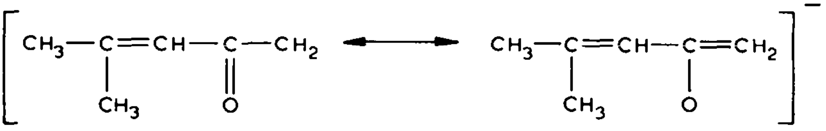
Fig. 2. Perspective view of the [Co(Me$_2$CO)$_2$(TPyEA)]$^{2+}$ cation.

the diacetone alcohol formed was found to be coordinated to the metal [2].

In spite of the previous arguments it is possible to exclude, on the basis of spectral evidence, that either diacetone alcohol or mesityl oxide is the acetone rearrangement product which is coordinated to the metal atom in complexes II and III. In fact, the bands near 1620 cm^{-1} in the infrared spectra of compounds II and III are hardly reconcilable with the $\nu(CO)$ band at 1715 cm^{-1} in the spectrum of the free molecule of diacetone alcohol *. On the other hand, no $\nu(OH)$ band appears in the spectrum of the free mesityl oxide molecule.

The present experimental results and the previously reported rearrangement modes of coordinated acetone molecules [2,8] could be reconciled by assuming that thermal condensation in the solid state of the two acetone molecules coordinated in complex I leads to the enol form of mesityl oxide (2-hydroxy-4-methylpentadiene) which is bound to the metal atom through its OH group. An analogous process, catalysed by water molecules, seems to take place at room temperature, leading to complex III.

In an attempt to test the above hypothesis, the bis-acetone complex was reacted with mesityl oxide. However, this reaction did not yield compound II or III but a new magenta complex of cobalt(II), hereafter referred to as compound IV. Its infrared spectrum differs from those of complexes II or III in having a strong band at 1591 cm^{-1} and no bands in the 1600–1700 and 3500 cm^{-1} regions (Fig. 1(d)). Moreover, the analytical data for complex IV suggest the presence of only one BPh_4^- anion. Consequently an anionic species must be present in the coordination sphere. Actually, the strong band at 1591 cm^{-1} is typical of the stretching mode of a C=O group involved in a resonance system [5,9] such as that, which could occur in a deprotonated form of mesityl oxide (Scheme 1).



$$\left[CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{O}{\underset{\|}{C}}-CH_2 \longleftrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{O}{\underset{|}{C}}=CH_2 \right]^-$$

SCHEME 1

The formation and coordination to the metal of deprotonated forms of mesityl oxide have previously been suggested to occur in solutions of the iridium complex $[Ir(C_5Me_5)(Me_2CO)_3]$ [4]. The formation of the present compound IV seems to be due to its fairly high stability, as indicated by the facts that: (a) the compound is obtained by different routes, e.g., also by refluxing an acetone/ethanol solution of I in presence of KCN (see Experimental); (b) it can be recrystallized, apparently unchanged, from its acetone solution, in contrast to compounds II and III, which revert to the bis-acetone complex I upon recrystallization from acetone.

Experimental

Preparation of the complex $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ (I)

The preparation of the ligand TPyEA has been described elsewhere [5]. Complex

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[*] Such difference in frequencies is much larger than that (viz. 40 cm^{-1}) found for the free and the coordinated solvent molecule in the mono-solvent adduct $[Co(solvent)(TPyEA)](BPh_4)_2$ (solvent = butan-2-one), which was synthesized for comparison purposes.

I was prepared as follows. A warm solution in acetone (20 cm^3) of the ligand in 10% excess over the stoichiometric ratio was added to a warm solution in ethanol (25 cm^3) of $[Co(H_2O)_6](ClO_4)_2$ (2×10^{-3} mol). A solution of an excess of $NaBPh_4$ in ethanol (15 cm^3) was then added and the mixture was allowed to evaporate slowly at room temperature until red crystals separated.

Anal. Found: C, 74.93; H, 6.87; N, 8.65. $C_{69}H_{73}N_7B_2O_2Co$ calcd.: C, 74.47; H, 6.61; N, 8.80%.

Reactions of complex I

A saturated solution of complex I in acetone (10 cm^3) was refluxed for several hours ($\leqslant$ 24 h). The organic liquid was distilled off and analyzed by means of GLC, solutions of authentic diacetone alcohol and mesityl oxide in acetone being employed for comparisons.

Complex II was obtained by heating of complex I under vacuum (5 mmHg) at 65°C for 24 h and subsequent cooling to room temperature in a dessiccator. The colour of the compound changes during the heating from deep red to magenta. A typical analysis is: C, 73.9; H, 6.51; N, 9.54%.

Complex III was obtained by leaving complex I in a water-saturated atmosphere at room temperature for 12 h, after which the initially red complex had turned magenta. The complex was then dried in a dessiccator under vacuum. A typical analysis is: C, 74.1; H, 6.22; N, 9.80%.

Samples of complex IV were obtained by two quite different experimental routes. In one case complex I was dissolved in warm mesityl oxide at temperatures < 60°C. After dissolution was complete a magenta crystalline product began to crystallize. Crystallization was completed by adding diethyl ether.

In a separate experiment complex I was dissolved in an acetone/ethanol solution containing a molar equivalent of solid KCN and the mixture was refluxed for 2 h then filtered. The solution was concentrated to a small volume and ethanol was added to give magenta crystals of complex IV. Complex IV can be recrystallized, apparently unchanged, from acetone/diethyl ether or nitroethane/diethyl ether. A typical analysis is: C, 63.2; H, 5.50; N, 13.0; Co, 7.00%.

Physical measurements

The apparatus and experimental techniques used for magnetic measurements, electronic and infrared spectra have been described previously [10]. Gas chromatographic analyses were carried out with a Hewlett Packard model 5750 Research Chromatograph.

TABLE 2

DETAILS OF DATA COLLECTION FOR $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$

Scan type	θ-2θ
Scan width (°)	$1.10+0.30 \tan \theta$
Scan speed (° min^{-1})	9
2θ limits (°)	5–50
No. of data	10,510
No. of data with $I > 3.5\sigma(I)$	3949

TABLE 3

POSITIONAL PARAMETERS ($\times 10^4$) FOR ATOMS BELONGING TO THE CATION IN THE STRUCTURE OF $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ [a]

Atom	*x*	*y*	*z*
Co	2304(1)	2510(1)	517(1)
O(1)	1869(3)	662(3)	−749(4)
O(2)	3312(3)	2031(4)	−98(4)
N(1)	2801(3)	4281(4)	1833(4)
N(2)	2690(3)	1932(4)	1675(4)
N(3)	1360(3)	2737(4)	876(4)
N(4)	2077(3)	2863(4)	−839(4)
N(5)	3302(3)	2379(4)	2508(4)
N(6)	1263(3)	3643(4)	1834(4)
N(7)	2533(4)	3822(4)	−671(4)
C(1)	3339(4)	4325(4)	2984(5)
C(2)	3695(4)	3444(4)	2796(4)
C(3)	3436(3)	1773(4)	3072(4)
C(4)	2917(4)	880(4)	2606(4)
C(5)	2456(3)	1003(4)	1735(4)
C(6)	2315(3)	5001(4)	2419(4)
C(7)	1834(3)	4390(4)	2784(4)
C(8)	589(3)	3713(4)	1763(4)
C(9)	227(3)	2837(4)	712(4)
C(10)	718(3)	2239(4)	170(4)
C(11)	3202(4)	4844(5)	1421(5)
C(12)	2787(4)	4936(4)	453(4)
C(13)	2400(4)	3656(4)	−1733(5)
C(14)	1935(4)	2784(4)	−2600(4)
C(15)	1727(4)	2282(4)	−1934(4)
C(16)	1886(4)	−283(4)	−1536(4)
C(17)	1604(4)	−1386(4)	−1541(5)
C(18)	2184(4)	−422(5)	−2575(5)
C(19)	3711(4)	1436(4)	−539(4)
C(20)	4068(4)	1645(5)	−1278(5)
C(21)	3832(4)	396(5)	−330(5)

[a] Standard deviations of the last significant digits are in parentheses. Atoms O(1), O(2) and C(16)–C(21) belong to the acetone molecules.

Mass spectra were obtained from a Kratos MS80 mass spectrometer with an ionizing voltage of 70 eV and source temperatures from 20 to 200°C.

Collection and reduction of X-ray data for $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$

Crystals of the compound decompose slowly in the air but faster when exposed to the X-rays. Several sets of diffraction data were collected under different conditions. The set considered most satisfactory and used for structure determination was obtained from a moderately large crystal (0.30 × 0.40 × 0.50 mm) at a rather high scan speed. A four-circle Philips PW 1100 automated diffractometer and graphite-monochromated Mo-K_α radiation (λ 0.71069 Å) were used for all operations. Cell parameters were determined from the setting angles of 24 reflections with $14 < \theta < 16°$.

Crystal data: triclinic, space group $P\bar{1}$; a 20.159(10), b 13.200(7), c 13.359(8) Å; α

TABLE 4

POSITIONAL PARAMETERS ($\times 10^4$) AND TEMPERATURE FACTORS ($\times 10^3$) FOR ATOMS BELONGING TO THE ANIONS IN THE STRUCTURE OF $[Co(Me_2CO)_2(TPyEA)](BPh_4)_2$ [a]

Atom	*x*	*y*	*z*	U (Å^2)
B(1)	6323(3)	4405(4)	2833(4)	42(1)
C(22)	6146(3)	3373(4)	3128(4)	43(1)
C(23)	5523(3)	2640(4)	2557(4)	56(1)
C(24)	5335(3)	1703(4)	2721(4)	60(1)
C(25)	5802(3)	1496(4)	3504(4)	61(1)
C(26)	6419(3)	2181(4)	4087(4)	60(1)
C(27)	6590(3)	3128(4)	3916(4)	53(1)
C(28)	7126(3)	5057(4)	3532(4)	42(1)
C(29)	7698(3)	4542(4)	3217(4)	52(1)
C(30)	8375(3)	5079(4)	3829(4)	62(1)
C(31)	8517(3)	6154(4)	4786(4)	67(1)
C(32)	7969(3)	6715(4)	5133(4)	66(1)
C(33)	7301(3)	6157(4)	4511(4)	55(1)
C(34)	5812(3)	5398(4)	3280(4)	43(1)
C(35)	5364(3)	5431(4)	3951(4)	44(1)
C(36)	4965(3)	6316(4)	4368(4)	52(1)
C(37)	5006(3)	7197(4)	4105(4)	58(1)
C(38)	5447(3)	7209(4)	3447(4)	57(1)
C(39)	5846(3)	6337(4)	3057(4)	51(1)
C(40)	6185(3)	3782(4)	1409(4)	49(1)
C(41)	5757(3)	4092(4)	661(4)	63(1)
C(42)	5627(4)	3488(4)	−584(4)	83(1)
C(43)	5928(4)	2556(4)	−1077(4)	85(1)
C(44)	6346(4)	2143(4)	−433(4)	86(1)
C(45)	6469(3)	2769(4)	806(4)	71(1)
B(2)	8676(3)	1803(4)	7191(4)	45(1)
C(46)	8966(3)	2403(4)	6487(4)	43(1)
C(47)	8534(3)	2588(4)	5653(4)	53(1)
C(48)	8786(3)	3162(4)	5107(4)	64(1)
C(49)	9482(3)	3539(4)	5407(4)	65(1)
C(50)	9921(3)	3362(4)	6206(4)	65(1)
C(51)	9661(3)	2792(4)	6746(4)	55(1)
C(52)	8703(3)	2804(4)	8516(4)	41(1)
C(53)	9066(3)	3927(4)	9054(4)	43(1)
C(54)	9109(3)	4768(4)	10215(4)	58(1)
C(55)	8757(3)	4518(4)	10867(4)	59(1)
C(56)	8374(3)	3432(4)	10368(4)	57(1)
C(57)	8339(3)	2603(4)	9218(4)	50(1)
C(58)	7877(3)	1142(4)	6459(4)	44(1)
C(59)	7299(3)	1666(4)	6749(4)	51(1)
C(60)	6612(3)	1106(4)	6118(4)	60(1)
C(61)	6497(3)	−6(4)	5165(4)	67(1)
C(62)	7059(3)	−557(4)	4844(4)	72(1)
C(63)	7748(3)	6(4)	5483(4)	61(1)
C(64)	9144(3)	801(4)	7222(4)	53(1)
C(65)	9532(4)	252(4)	6380(4)	80(1)
C(66)	9883(4)	−719(4)	6357(4)	100(1)
C(67)	9830(4)	−1105(4)	7125(4)	94(1)
C(68)	9476(4)	−573(4)	7967(4)	85(1)
C(69)	9137(3)	389(4)	8026(4)	68(1)

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[a] Standard deviations of the last significant digits are in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$.

117.77(8), β 102.53(9), γ 91.81(8)°; V 3034.0 Å^3; $Z = 2$; ρ(calc) 1.218 g cm^{-3}; μ(Mo-K_α) 3.29 cm^{-1}.

Details of data collection are given in Table 2. The intensities of 3 standard reflections monitored every 120 min showed a smooth decay with a 20% overall decrease. Data properly rescaled were corrected for absorption and for the Lorentz and polarization effects. A 0.05 value of the "ignorance" factor was used in the reduction of data [11]. All calculations were performed on a SEL 32/70 computer with the programs described in ref. [12]. Scattering factors for the neutral atoms and the anomalous dispersion correction for the metal atom were taken from ref. [13].

Solution and refinement of the structure

The position of the Co atom was found by a Patterson synthesis and those of the other non-hydrogen atoms were determined from Fourier maps. The structure was refined using large-block (ca. 270 parameters) least squares in which the function $\Sigma w(|F_0| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2\ (F_0)$. In the final cycles, in which only reflections with $I > 3.5\sigma(I)$ were employed, all atoms heavier than hydrogen in the cation were assigned anisotropic temperature factors whereas atoms of the anions were refined isotropically. Hydrogen atoms were entered in calculated positions (C–H 1.00 Å, temperature factors close to those of the atoms to which they are attached) and not refined. The refinement converged at $R = 0.081$ and $R_w = 0.086$, where $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$. Differences larger than 3σ existing between various chemically equivalent bonds and angles in the structure are attributed to systematic errors in the data as a result of decomposition. The positional and thermal parameters of the atoms (N(4), N(7), C(11)–C(15)) forming one arm of the TPyEA ligand are particularly affected by decomposition and/or disorder. The highest peaks ($\leqslant 0.6$ e Å^{-3}) in the final ΔF map are located in the region of this arm. In spite of the difficulties, we believe that the present structure determination provides sufficiently accurate information to reveal the important chemical features.

Final atomic parameters are listed in Tables 3 and 4. Listings of the anisotropic temperature factors and of structure factor amplitudes are available from the authors on request.

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