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Tris(3-methyl-2,4-pentanedionato-*O*,*O*′)-cobalt(III)

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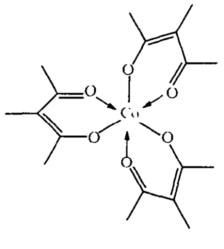
Abstract

Examination of two crystalline forms of tris(methylacetylacetonato)cobalt(III), [Co($C_6H_9O_2$)$_3$], indicate that the cobalt ion is coordinated by three chelating ligands resulting in octahedral complexes. The first crystal form is cubic with the Co atom lying on a threefold axis, and the crystal contains a small amount (~1.65 molecules) of disordered water. The second crystal form is triclinic with two unique complexes.

Comment

In an investigation of mixed-ligand cobalt(III) complexes of the ligand 2-(*N*-methylamino)benzimidazole, it was shown that methylacetylacetonato (Meacac) complexes could not be isolated, despite the successful preparation of the acetylacetonato (acac) analogues (Cardwell *et al.*, 1997). These observations could be accounted for by destabilization of cobalt(III) complexes of Meacac relative to those of acac. It was thought that the 2- and 4-methyl groups may be forced towards the 3-methyl group upon chelation as the O atoms separate to accommodate the metal ion. If the influence of the 3-methyl group on the stability of these complexes was steric in origin, then this should be revealed by a comparison of the structure of [Co(Meacac)$_3$] with that of [Co(acac)$_3$]. For this reason, we have examined the structure of [Co(Meacac)$_3$].



[Co(Meacac)$_3$]

Crystal structure determinations were undertaken on two crystals taken from an aqueous methanol solution. The first structure, (I) (Fig. 1), is cubic with the Co atom lying on a threefold axis, which is not unexpected given the 'propeller'-type structure adopted by the complex with its three chelating ligands. In addition to the complex, the crystal contains a small amount of disordered water (~1.65 molecules). The second crystal form, (II) (Fig. 2), is triclinic with two unique complexes. Both complexes have a similar 'propeller'-type arrangement. Despite the different symmetry of the crystals, the geometry of each of the complexes is very similar. The Co—O distances are in the range 1.868 (5)–1.887 (5) Å. The chelating ligands have bite angles in the range 94.2 (2)–95.2 (2)°. The inter-ligand O—Co—O angles are in the range 87.1 (2)–90.4 (4)° for *cis*-O atoms and in the range 174.4 (2)–177.3 (2)° for *trans*-O atoms. The geometry of the Meacac ligand in each complex is similar to that observed for the acac ligand in [Co(acac)$_3$] (Kruger & Reynhardt, 1974; Hon & Pfluger, 1973; Wright & Meyers, 1980). It thus appears that the central methyl group exerts only a minor steric influence.

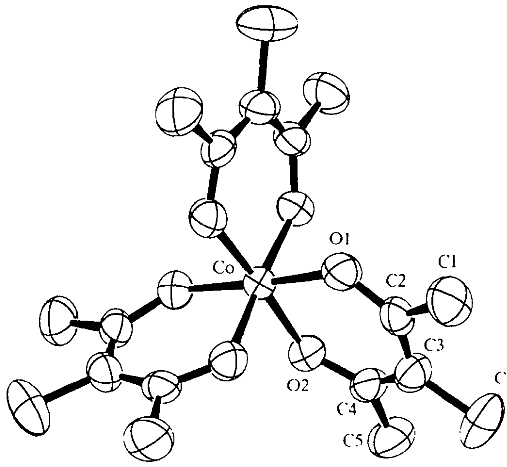


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (I). Displacement ellipsoids are at the 50% probability level. A threefold axis passes through the Co atom.

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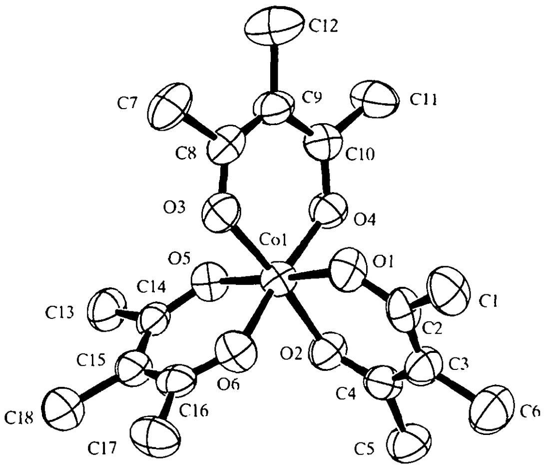

Fig. 2. *ORTEP*II (Johnson, 1976) diagram of one of the two independent molecules in the asymmetric unit of (II). Displacement ellipsoids are at the 50% probability level.

Experimental

The complex tris(methylacetylacetonato)cobalt(III) was prepared by addition of methylacetylacetone to potassium hexanitritocobalt(III). Cubic and triclinic crystals were obtained by slow evaporation of a water–methanol solution.

Compound (I)

Crystal data

$[Co(C_6H_9O_2)_3].1.65H_2O$
$M_r = 428.07$
Cubic
$P\bar{4}3n$
$a = 16.476\,(1)$ Å
$V = 4472.6\,(5)$ Å^3
$Z = 8$
$D_x = 1.272$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 16.5$–$31.6°$
$\mu = 6.325$ mm^{-1}
$T = 293\,(2)$ K
Rectangular prism
0.51 × 0.39 × 0.34 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical, indexed crystal faces (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.095$, $T_{max} = 0.259$
5398 measured reflections
1008 independent reflections

771 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 74.95°$
$h = -1 \rightarrow 20$
$k = -6 \rightarrow 20$
$l = -3 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.158$
$S = 1.138$
1007 reflections
92 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 0.9998P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.408$ e Å^{-3}
$\Delta\rho_{min} = -0.264$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (2)

Compound (II)

Crystal data

$[Co(C_6H_9O_2)_3]$
$M_r = 398.34$
Triclinic
$P\bar{1}$
$a = 8.0403\,(6)$ Å
$b = 15.1514\,(11)$ Å
$c = 16.4575\,(10)$ Å
$\alpha = 108.076\,(6)°$
$\beta = 90.971\,(6)°$
$\gamma = 96.484\,(7)°$
$V = 1890.9\,(2)$ Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 7.7$–$23.8°$
$\mu = 7.374$ mm^{-1}
$T = 293\,(2)$ K
Rectangular prism
0.23 × 0.13 × 0.06 mm
Dark green

Data collection

Enraf–Nonius CAD-4F diffractometer
ω–2θ scans
Absorption correction: analytical, indexed crystal faces (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.335$, $T_{max} = 0.675$
7920 measured reflections
7156 independent reflections

3522 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 69.90°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 17$
$l = -1 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.083$
$wR(F^2) = 0.239$
$S = 1.035$
7153 reflections
476 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1080P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.733$ e Å^{-3}
$\Delta\rho_{min} = -0.726$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0010 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The triclinic crystal was only weakly scattering and this is largely responsible for the elevated R values associated with the structure. In both structures, the methyl H atoms appeared to be disordered. For each methyl group, the H atoms were included at two sets of geometrically calculated sites rotated by 60° relative to each other.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *PROCESS_DATA* (Gable *et al.*, 1993); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1026). Services for accessing these data are described at the back of the journal.

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Bis[bis(ethylenediamine-N,N')($\mu_{N,S}$-thiocyanato)nickel(II)] Bis(hexafluorophosphate)

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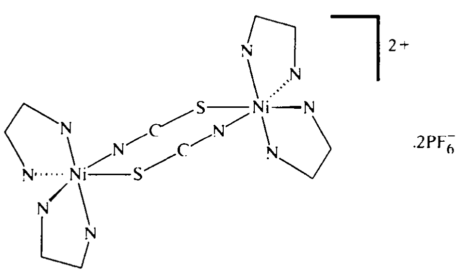
Abstract

The title compound, $[Ni_2(NCS)_2(C_2H_8N_2)_4](PF_6)_2$ or $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2[PF_6]_2$ (en = ethylenediamine), has been synthesized *via* a molecular rearrangement reaction of *trans*-$Ni(en)_2(NCS)_2$. It consists of dibridged $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2$ cations with the NCS ligands forming a *cis* arrangement at the nickel centres. A three-dimensional intermolecular hydrogen-bonding network is observed between the amine protons of the en ligands and the F atoms of the PF_6^- anions.

Comment

The cationic component of the title compound, (1), consists of a pair of pseudo-octahedrally coordinated Ni atoms, linked by two bridging thiocyanato ligands to give a dimeric species. The symmetry of (1) is such as to place a crystallographic inversion centre at the centre of the dimer. Hexafluorophosphate groups form the anionic component of this complex salt, with each PF_6^- group sitting on a crystallographic twofold axis. The arrangement of these ions in the asymmetric unit of (1) is shown in Fig. 1. As may be noted from this figure, the two thiocyanate bridges of (1) show only slight deviations from coplanarity. The dihedral angle formed by the planes containing atoms Ni1, S1, C1 and Ni1, S1, N1 is 3.5 (1)°.



(1)

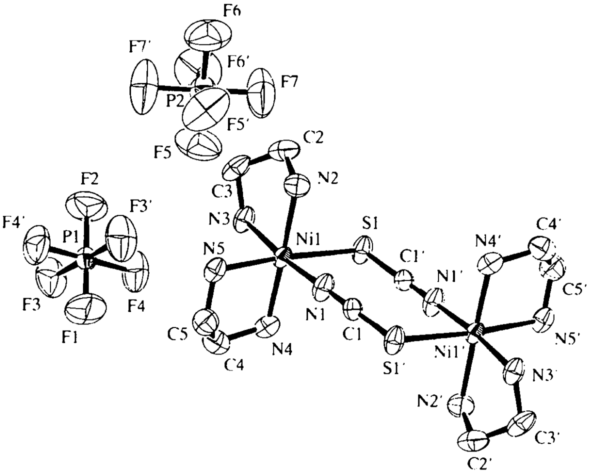


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2[PF_6]_2$, (1). All atoms are represented by 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The analogous iodide and perchlorate salts of (1) have previously been communicated (Svelasvili, 1966); however, this is the first report of a salt containing the PF_6^- counter-ion. Other related dithiocyanato-bridged species have been observed, notably for $[Ni(tren)_2(\mu_{N,S}\text{-}NCS)]_2[BPh_4]_2$ (tren = 2,2′,2″-triaminotriethylamine; Duggan & Hendrickson, 1974),

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