

단 신

아세테이트 다리결합 리간드의 선형 삼핵 코발트(II) 착물: 헥사키스아세타토디페난트로린코발트(II)

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(2003. 9. 15 접수)

A Linear Trinuclear Cobalt(II) Complex with Acetate Bridging Ligand: Hexakisacetatodiphenanthrolinetricobalt(II)

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(Received September 15, 2003)

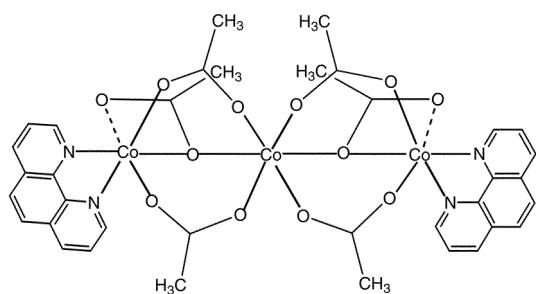
주제어: 선형, 삼핵, 코발트(II)-아세테이트 착물, 결정구조

Keywords: Linear, Trinuclear, Cobalt(II)-acetate complex, Crystal structure

Metal carboxylate chemistry has been received much attention in several different fields ranging from catalysis¹ to bioinorganic² and materials chemistry.³ Their clusters have often the aesthetically fascinating structures and exhibit unusual magnetic properties.⁴ Previously, numerous trinuclear carboxylate complexes have been reported.⁵ However, the dominant structure in trinuclear metal carboxylate complexes is the oxo-centered equilateral triangle of the basic carboxylates, $[M_3(\mu_3-O)(O_2CCH_3)_6L_3]^{n+}$ ($M = Co$, $L = py$, $n = 0, 1$)⁶ and a few linear type of the structure has been known. Especially, it is rare that the carboxylate functions primarily as a monoatomic ($M-O-M$) bridge. Recently, Mn - and Fe - acetate complexes with a linear trinuclear structure of the type $[M_3(O_2CCH_3)_6L_2]$ ($M = Mn$, Fe, and $L = BIphMe$, phen) have been synthesized⁷ from the reactions of Mn (II) - or Fe (II) - acetates with 2,2'-bis(1-methylimidazolyl)-phenylmethoxymethane (BIphMe) or 1,10-phenanthroline (phen) for Mn and 2,2'-bis(1-methylimidazolyl)phenylmethoxymethane for Fe. Also, a linear trinuclear mixed oxidation

state cobalt (III/II/III) complex with pyrazolate bridges has been prepared.⁸

While attempting to synthesize a linear trinuclear metal (II) complexes which bind acetates in the manner proposed above for the low valent metal - cobalt (II), copper (II), and nickel (II) *et al.*, we obtained the title compound $[Co_3(O_2CCH_3)_6(phen)_2]$ (1) and its structure is presented here.



Scheme 1.

The constitution of the trinuclear complex was checked primarily by the physicochemical methods (see experimental section). The resulting data are

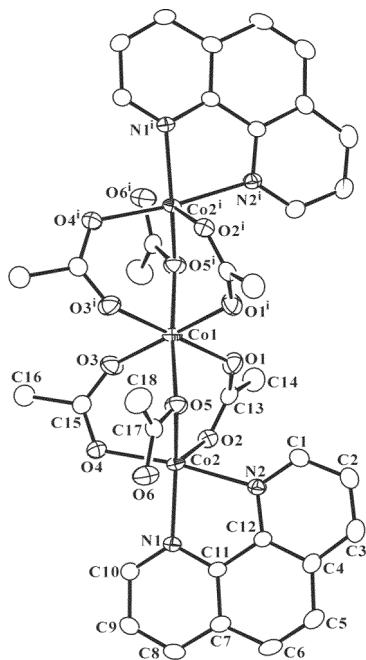


Fig. 1. ORTEPIII¹⁴ drawing of 1. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) 1-x, y, 1/2-z].

consistent with the molecular formula as $\text{Co}_3(\text{O}_2\text{CCH}_3)_6(\text{phen})_2$. The infrared spectroscopy exhibits two characteristic bands at *ca.* 1,600 and 1,420 cm^{-1} due to $\nu_{\text{asym COO}^-}$ and $\nu_{\text{sym COO}^-}$ of all bridging acetates, respectively. A similar result was observed in related complexes containing bridged carboxylates.⁹

The crystal structure of 1, shown in Fig. 1, consists of a linear trinuclear array of $\text{Co}(\text{O}_2\text{CCH}_3)_3\text{Co}(\text{O}_2\text{CCH}_3)_3\text{Co}$ unit. The central cobalt, Co1, which is located on an inversion center in space group C2/c, is coordinated octahedrally by six acetate oxygen atoms, while two terminal cobalts, Co2 and Co2ⁱ are 5-coordinate i.e trigonal bipyramidal geometries and are capped by phen ligands, respectively. Four acetate groups form bridges to the two flanking cobalts in the bidentate fashion [$\text{Co}-\text{O}_{\text{av}}=2.073(4)$ Å], whereas the other two act as monodentate [$\text{Co}-\text{O}_{\text{av}}=2.091(4)$ Å]. The orientation of the bidentate phenanthroline ligands lies on the same sides with respect to the plane defined by the O6 in monodentate acetate and Co2 atoms. The central cobalt atom, Co1 is on the least squares plane (mean deviation is 0.006 Å)

formed by the four oxygen atoms of acetates, while the terminal cobalt atom, Co2 is displaced out of the plane, O5-O2-O6-N1 (mean deviation is 0.064 Å) toward the N2 atom of phen by 0.143 Å. The bridging angle Co1-O5-Co2 is 107.0(2) $^\circ$; this is in the range 103.2(1)-107.4(1) $^\circ$ reported for other trinuclear transition metal complexes containing two monoatomic bridging acetates.¹⁰

Monodentate acetates coordinate one oxygen atom as a monoatomic bridge between the cobalts, while the second oxygen atom is dangling atom which interacts weakly with the terminal cobalt. Such existence of a weak interaction between the dangling oxygen atoms O6 and O6ⁱ and the terminal cobalts Co2 and Co2ⁱ is well described in previously reported complex $[\text{Mn}_3(\text{O}_2\text{CCH}_3)_6(\text{phen})_2]$.⁷ The presence of monodentate bridging acetates results in a significant difference between the length of the two carboxylate CO bonds, the C17-O5 distance [1.277(6) Å] being longer than the C17-O6 distance [1.233(7) Å]. The Co2-O6 distance is 2.421(5) Å and the monodentate acetates are oriented such that O6 and O6ⁱ point toward terminal cobalts as manifested in the Co2-O5-C17 angle [101.7(4) $^\circ$] being significantly smaller than Co1-O5-C17 [139.8(4) $^\circ$]. Also, the trigonal - bipyramidal coordination geometry of the terminal cobalts is distorted toward octahedral geometry. This distortion is well supported by the N1-Co2-O5 angle in trigonal plane which is bisected by the Co2-O6 vector. The angle is 140.9 (2) $^\circ$ which is a striking departure from the idealized trigonal - bipyramidal value of 120 $^\circ$.

The bidentate acetate bridges are highly twisted with a Co1-O1-C13-O2 and a O1-C13-O2-Co2 of torsional angles of -50.2(0.8) $^\circ$ and -1.6(0.8) $^\circ$, respectively. Monodentate acetate plane is nearly plane (mean deviation is 0.003 Å) and the dihedral angle to the plane, Co1-O5-Co2 is 28.2(0.2) $^\circ$. The torsional angle of Co(1)-O(5)-Co(2)-N(1) is -173.6(2) $^\circ$ and the Co(1)-Co(2) distance is 3.361(0.8) Å.

The redox property of 1 in aqueous solution has been studied by cyclic voltammetric technique. The complex displays an irreversible reduction wave at -644 mV vs Ag/AgCl (Fig. 2) due to the reduction of Co(II) to Co(I). This electrochemical behaviour

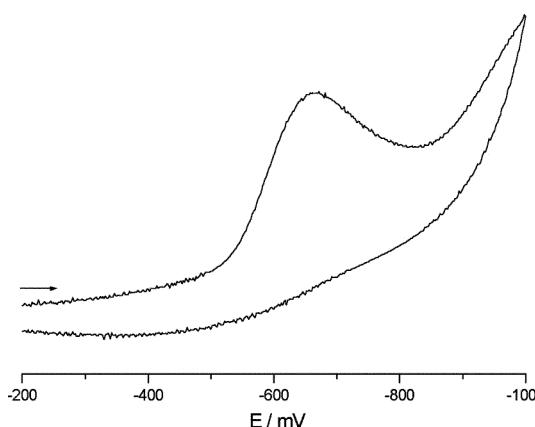


Fig. 2. Cyclic voltammogram of 1 in an aqueous solution containing 0.1 M TEAP as a supporting electrolyte. The voltammogram was generated using a platinum working electrode and platinum wire counter electrode and is referenced against an Ag/AgCl electrode at 50 mV/s.

is similar to that of the monomer complex $[\text{CoCl}_2(\text{triphos})]$ [triphos=1,1,1 tris(diphenylphosphino)methylene]¹⁵ having the oxidation state +2. So, it would seem that the structure of the complex is destroyed to monomer in the solution.

Table 1. Crystal Data and Structure Refinement for Compound 1

Empirical formula	$\text{C}_{36}\text{H}_{34}\text{Co}_3\text{N}_4\text{O}_{12}$
Formular weight	891.46
Crystal system, Space group	<i>Monoclinic, C 2/c</i>
Unit cell dimensions	$a=11.351(2)\text{\AA}$, $b=12.318(2)\text{\AA}$, $\beta=98.23(1)^\circ$ $c=26.020(4)\text{\AA}$, $3601(1)\text{\AA}^3$
Volume	
Z , Calculated density	4, 1.644 Mg/m^{-3}
μ (mm^{-1} with Mo-K α)	1.437 mm^{-1}
θ range for data collection	1.58 to 27.48°
Index ranges	$-14 \leq l \leq 14$, $0 \leq k \leq 15$, $0 \leq l \leq 33$
Reflections collected/unique	4114/4114
Completeness to 2θ	99.6%
Absorption correction (T_{\min}/T_{\max})	Numerical (0.7745/0.9082)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4114/0/249
Final R indices [$I > 2\sigma(I)$, 2508]	$R_1=0.0614$, $wR_2^a=0.1206$
R indices (all data)	$R_1=0.1192$, $wR_2^a=0.1560$
Goodness-of-fit on F^2	1.129
Largest diff. peak and hole	1.020 and -0.482 e\AA^{-3}

^a $w=1/[\sigma^2(F_o^2)+(0.0451P)^2+17.2917P]$ where $P=(F_o^2+2F_c^2)/3$

EXPERIMENTAL

To a stirred solution of $\text{Co}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.04 mmol, 0.508 g) in 20 ml of DMF was added a solution of 1,10-phenanthroline (1.36 mmol, 0.27 g) in 10 ml of DMF. The resulting solution was allowed to stir for 10 min. and then pink solid began to precipitate. After stirring for further 10 min, the reaction mixture was filtered off and washed with several aliquots of DMF, followed by several aliquots of acetone, and then diethyl ether. The solid was dried in vacuo. Data for (1): Yield 0.38 g (62%). mp=297 °C (dec.). λ_M ($\mu\text{mho cm}^2\text{ mol}^{-1}$, in DMSO at 25 °C): 28. Anal. Calc. for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_{12}\text{Co}_3$: C, 48.50; H, 3.84; N, 6.28; Co, 20.95. Found: C, 48.07; H, 3.86; N, 6.39; Co, 20.60. FAB-MS, m/z: $[\text{M}+2\text{H}]^+$, 893; $[\text{M}-\text{OAc}+\text{H}]^+$, 833; $[\text{M}-\text{phen}+2\text{H}]^+$, 713. FT-IR (KBr, cm^{-1}): 3069, 2923, 1592 ('asym. COO⁻'), 1515, 1419 ('sym. COO⁻'), 1339, 1018, 849, 728, 669.

Pink crystals of (1) suitable for X-ray diffraction study were grown by diffusive mixing of DMF solutions of 1,10-phenanthroline and $\text{Co}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$.

Table 2. Selected geometric parameters (\AA , $^\circ$).

Co1-O1	2.110 (4)	Co2-N2	2.159 (4)
Co1-O3	2.071 (4)	O1-C13	1.248 (7)
Co1-Co2	3.3608 (8)	O2-C13	1.258 (7)
Co1-O5	2.097 (4)	O5-C17	1.277 (6)
Co2-O2	2.050 (4)	O6-C17	1.233 (7)
Co2-O4	2.062 (4)	N1-C10	1.325 (7)
Co2-O5	2.085 (4)	C1-C2	1.391 (8)
Co2-O6	2.421 (5)	C13-C14	1.504 (8)
Co2-N1	2.107 (4)	C17-C18	1.468 (9)
O1-Co1-O1 ⁱ	91.2 (2)	O5-C17-O6	115.4 (6)
O1-Co1-O3	91.5 (2)	O5-C17-C18	122.5 (6)
O3-Co1-O3 ⁱ	85.9 (3)	O6-C17-C18	122.0 (5)
O3 ^j -Co1-O1 ⁱ	91.5 (2)	O2-Co2-O4	95.2 (2)
O1-Co1-O5	87.9 (2)	O2-Co2-O5	112.0 (2)
O1-Co1-O3 ⁱ	176.8 (2)	O2-Co2-N1	104.8 (2)
O5-Co1-O5 ⁱ	175.5 (2)	O2-Co2-N2	88.1 (2)
Co1-O5-Co2	107.0 (2)	O5-Co2-N1	140.9 (2)
O1-C13-O2	127.3 (5)	O4-Co2-N2	173.6 (2)
O1-C13-C14	116.3 (6)	N1-Co2-N2	77.4 (2)

Symmetry transformations of i: 1-x, y, -z+1/2

Crystal Structure Determination of 1. X-ray quality crystals were obtained as described above. A crystal size 0.50×0.25×0.13 mm was used for data collection on a STOE STAD14 four-circle-diffractometer¹¹ with graphite-monochromatized Mo-K α radiation ($\lambda=0.71069 \text{ \AA}$) at room temperature. Cell parameters and orientation matrix for data collection were determined by least-squares refinement, using 34 reflections in the range of $9.5^\circ < \theta < 10.5^\circ$. Data were collected using the ω -2 θ scan technique. Three standard reflections monitored every 1h and decayed 4.4% over the course of the data collection. The intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct method¹² and refined by full-matrix least-squares methods.¹³ All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized ($d(\text{C-H})=0.93$ or 0.96 \AA) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of attached atom. The data collection and structure solution parameters are listed in Table 1, together with standard discrep-

ancy indices R and wR .

This work was partially supported by the 2003 research fund of Catholic University of Daegu, Korea.

Supporting information available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-216817). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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