Low-Temperature X-Ray Structural Investigation of $[Mn^{II}(1,10\text{-}C_{12}H_8N_2)_3]^{2+}[Co^{III}(\pi\text{-}1,2\text{-}C_2B_9H_{11})_2]_2^-$

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Abstract

The crystal structure of [] is determined by means of X-ray structural analysis at 190(2) K. Crystals are monoclinic, space group $P2_1/n$, $a = 16.7983(5)$, $b = 15.1424(5)$, $c = 24.6255(7)$ Å, $\beta = 102.006(1)°$, $Z = 4$, $d_{calc} = 1.348$ g/cm^3, $R = 0.0266$ (autodiffractometer Nonius KAPPA CCD, λMoK_α, 11969 independent reflections. Crystals are built of the cations $[Mn^{II}(1,10\text{-}C_{12}H_8N_2)_3]^{2+}$ and two crystallographically independent sorts of anions $[Co^{III}(C_2B_9H_{11})_2]^-$. Mn(II) atom has a distorted octahedral coordination formed by six nitrogen atoms of three phenanthroline molecules, with mean Mn—N bond length of 2.255(1) E. Each cluster anion is composed of two icosahedra having a common vertex which is occupied by the Co(III) atom in a "sandwich" position. One of the anions has a structure close to cisoid (quasi-gauche) position of dicarbollide clusters $(C_2B_9H_{11})^{2-}$ with respect to the C—C fragments and another – transoid. The decisive part in the stabilization of different conformations of the anion is played by the complex cation $Mn(C_{12}H_8N_2)_3$.

INTRODUCTION

Metal derivatives of *o*-carborane(12) containing a cluster ligand, *i. e.* dicarbolide anion $C_2B_9H_{11}^{2-}$, are of substantial interest as the structures possessing three-dimensional aromaticity which can be the reason of interesting physical properties (optical, magnetic, *etc.*). Specific interactions of electron systems with different types of aromaticity (plain and three-dimensional) are possible. Because of this, it was interesting to study a salt-like compound $[Mn^{II}(1,10\text{-}C_{12}H_8N_2)_3]^{2+}[Co^{III}(\pi\text{-}1,2\text{-}C_2B_9H_{11})_2]_2^-$ (**1**). Complex cation **1** contains paramagnetic atom Mn(II) and plain heterocyclic aromatic molecules of 1,10-phenanthroline (Phen) coordinated bidentately by their N atoms with the Mn(II) atom. The anion is a cobalt derivative of *o*-carborane(12). Co(III) atom occupies a "sandwich" position between cluster ligands $C_2B_9H_{11}^{2-}$. This anion system possesses a three-dimensional aromatic character with electron delocalization over the atoms of the clusters [1]. This anion can be called 3,3'-*commo*-bis-[η^5-undecahydro-1,2-dicarba-3-cobalt(III)-*closo*- dodecaborate](1−) further on referred to as $[Co(C_2B_9H_{11})_2]^-$ and bisdicarbollide complex of Co(III).
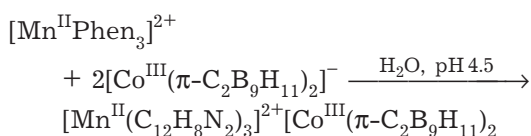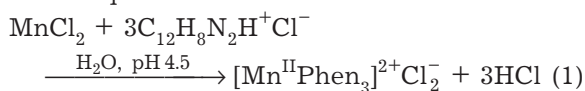
There is a series of publications concerning the structure of $[Co(C_2B_9H_{11})_2]^-$ anion and its salts [2, 3]. One of the features of "sandwich" structures of $[M^{n+}(C_2B_9H_{11})_2]^{n-2}$ complexes (where M^{n+} is a transition metal ion) is the ability to form different structural conformers determined by mutual position of C—C atom pairs in $C_2B_9H_{11}^{2-}$ ligands. A clearly exhibited transoid position of C—C pairs is observed in the $(CH_3)_4N^+[Ni^{III}(C_2B_9H_{11})_2]^-$ ligands [4]. On the other hand, in the molecular complex $[Ni^{IV}(C_2B_9H_{11})_2]^0$, a cisoid "sandwich" structure is realized for the C—C pairs [5] which causes a substantial dipole moment and the ability to form charge-transfer complexes. For the bisdicarbollide complex of Co(III) with Cs$^+$ cation, statistical disordering was observed for the two

B atoms and two C atoms over four crystallographic positions which did not allow to state conformer type unambiguously [2]. By the way, the results obtained can be interpreted in terms of the superposition of the conformer types. Cisoid structure was stated for the compound with the cation $(C_2H_5)_3NH^+$ [3]. Both investigations [2, 3] were conducted at room temperature. Consequently, important details of the structure of complexes under consideration depend on the cation component.

The goal of the present study is the investigation of Co(III) (**1**) at 190 K.

EXPERIMENTAL

A salt-like complex **1** was synthesized according to the known principles of the formation of $[MnPhen_3]^{2+}$ and deposition of $[Co(C_2B_9H_{11})_2]^-$ under the action of a large cation in aqueous medium:

$$MnCl_2 + 3C_{12}H_8N_2H^+Cl^-$$

$$\xrightarrow{\;H_2O,\ pH\,4.5\;} [Mn^{II}Phen_3]^{2+}Cl_2^- + 3HCl \quad (1)$$

$$[Mn^{II}Phen_3]^{2+}$$

$$+ 2[Co^{III}(\pi\text{-}C_2B_9H_{11})_2]^- \xrightarrow{\;H_2O,\ pH\,4.5\;}$$

$$[Mn^{II}(C_{12}H_8N_2)_3]^{2+}[Co^{III}(\pi\text{-}C_2B_9H_{11})_2]$$

A necessary condition for this reaction sequence to occur is weakly acidic aqueous reaction medium excluding the oxidation of Mn(II) to Mn(IV) and hydrolysis of Co(III) bisdicarbollide. Reactions were carried out in acetate buffer solution with pH 4.52. Complex **1** precipitated in water solution was prepared as a dark-yellow amorphous deposit with a yield of 90 %. Thus obtained **1** was then subjected to crystallization in the CH_3CN solution under the action of H_2O vapour diffusion in a tightly closed container; dark-red crystals of **1** were obtained which could be used in X-ray phase analysis.

The structure and chemical formula of **1** were determined by means of X-ray phase analysis using well-faced single crystals. The parameters of elementary cell and reflection intensities were obtained using a Nonius Kappa CCD autodiffractometer at 190 (2) K from the crystal of the dimensions $0.55 \times 0.39 \times 0.33$ mm using MoK_α radiation.

Crystallographic data for **1** are as follows: monoclinic syngony, $a = 16.7983(5)$, $b = 15.1424(5)$, $c = 24.6255(7)$ Å, $\beta = 102.006(1)^\circ$, $V = 6126.9(3)$ Å^3, $Z = 4$, $P2_1/n$, $d_{calc} = 1.348$ g/m^3, $\mu = 0.780$ mm^{-1}, $2\theta_{max} = 52^\circ$, 41 895 reflections were measured as a total, with $-20 \leq h \leq 20$, $-18 \leq k \leq 18$, $-30 \leq l \leq 30$ among which 11 969 were used in calculations. Intensities were corrected for the Lorentz factor and polarizations, the absorption was taken into account along the curve of azimuth scanning. The structure was deciphered directly and corrected with the full-matrix least squares method in the anisotropic/isotropic (for H atoms) approximation using the complex of programmes SHELX-97 [6]. The coordinates of H atoms in Phen molecules were fixed in calculated positions (C—H bond length 0.950 Å). 978 parameters of the structure were corrected till the final divergence factors: $R(F) = 0.0266$, $wR(F^2) = 0.0694$ using the reflections with $I > I > 2\sigma(I)$, $R(F) = 0.0317$, $wR(F^2) = 0.0743$ for all the reflections. The residual extremums (min/max) were 0.319 and -0.327 $e/$Å^3. Coordinates and equivalent isotropic heat parameters of atoms different from hydrogen are shown in Table 1 and the basic interatomic distances in Table 2. Anisotropic heat parameters and the coordinates of hydrogen atoms can be available from the authors on request.

RESULTS AND DISCUSSION

The complex structure is ionic. Crystals are built of the complex cations $Mn(Phen)_3^{2+}$ and two crystallographically independent anions of cobalt bis-dicarbollide $[Co(C_2B_9H_{11})_2]^-$. All the atoms of the structure occupy common positions. The geometry of ions with atom numbers is shown in Figs. 1 and 2.

Distorted octahedral surroundings of Mn(II) are formed by six nitrogen atoms of three Phen molecules. Mn—N bond lengths fall within a narrow range of 2.223(1)−2.278(1) Å. These figures are in fact identical to those stated for $[Mn(Phen)_3]^{2+}$ in the structure of $[Mn(Phen)_3]^{2+}[S_2P(OC_2H_5)]_2^-$ which were in the range of 2.224(18)−2.285(13), mean 2.257(14) Å

TABLE 1

Coordinates of atoms ($\times 10^4$) and equivalent isotropic heat parameters of atoms other than hydrogen
($\times 10^3$, $U_{equiv} = 1/3(U_{11} + U_{22} + U_{33})$) in $[Mn^{II}(1,10\text{-}C_{12}H_8N_2)_3]^{2+}[Co^{III}(\pi\text{-}1,2\text{-}C_2B_9H_{11})_2]_2^-$

Atom	x	y	z	U_{equiv}, Å^2
Mn(1)	8114.97(13)	6345.18(15)	926.33(9)	23.06(6)
N(1)	8713.9(8)	5004.4(8)	1033.9(5)	27.0(3)
N(2)	9305.9(7)	6493.7(8)	641.5(5)	25.2(3)
C(1)	8429.6(11)	4280.0(11)	1233.9(7)	35.2(4)
C(2)	8868.4(13)	3491.6(12)	1326.3(8)	44.1(4)
C(3)	9622.8(12)	3450.0(12)	1207.7(8)	43.2(4)
C(4)	9946.8(10)	4194.8(11)	991.2(7)	34.2(4)
C(5)	10 724.3(11)	4197.9(13)	839.2(8)	42.8(4)
C(6)	10 998.8(10)	4921.6(14)	622.6(7)	42.3(4)
C(7)	10 538.6(9)	5724.7(12)	543.8(6)	32.2(4)
C(8)	10 804.9(10)	6498.1(14)	321.5(7)	39.2(4)
C(9)	10 325.8(10)	7235.9(12)	256.1(7)	36.9(4)
C(10)	9580.4(10)	7206.2(11)	423.8(7)	32.0(3)
C(11)	9776.6(9)	5752.9(10)	696.9(6)	25.4(3)
C(12)	9469.4(9)	4968.4(10)	914.4(6)	26.0(3)
N(3)	8529.4(7)	6782.1(8)	1801.2(5)	26.3(3)
N(4)	7112.4(7)	5936.8(8)	1367.1(5)	26.8(3)
C(13)	9219.7(9)	7202.4(11)	2008.6(7)	32.4(3)
C(14)	9403.1(10)	7547.3(12)	2545.8(7)	36.6(4)
C(15)	8861.1(10)	7427.4(12)	2884.2(7)	35.5(4)
C(16)	8131.1(9)	6965.1(11)	2686.6(6)	28.7(3)
C(17)	7534.2(10)	6806.2(12)	3014.7(7)	35.3(4)
C(18)	6837.8(10)	6372.8(12)	2803.6(7)	35.2(4)
C(19)	6669.5(9)	6056.2(11)	2243.8(7)	29.0(3)
C(20)	5947.3(10)	5602.9(12)	2003.6(7)	35.9(4)
C(21)	5830.3(10)	5328.5(12)	1464.2(8)	37.5(4)
C(22)	6423.7(10)	5512.3(11)	1157.7(7)	32.1(3)
C(23)	7238.5(9)	6203.7(10)	1906.8(6)	24.8(3)
C(24)	7986.4(9)	6661.1(10)	2134.8(6)	24.0(3)
N(5)	7764.9(7)	7740.7(8)	622.0(5)	26.4(3)
N(6)	7331.6(7)	6189.7(8)	79.5(5)	24.2(3)
C(25)	7970.8(10)	8502.4(11)	883.5(7)	33.2(4)
C(26)	7781.9(10)	9327.5(11)	634.9(8)	38.3(4)
C(27)	7351.5(10)	9368.2(11)	104.8(8)	36.2(4)
C(28)	7094.6(9)	8581.1(10)	−186.1(7)	29.1(3)
C(29)	6612.1(10)	8563.4(11)	−738.2(7)	35.0(4)
C(30)	6403.1(10)	7798.3(12)	−1006.2(7)	34.2(4)
C(31)	6658.9(9)	6969.2(11)	−750.0(6)	28.3(3)
C(32)	6468.8(10)	6151.0(12)	−1018.5(7)	34.3(4)
C(33)	6693.6(10)	5383.6(12)	−734.9(7)	34.6(4)
C(34)	7119.6(9)	5435.0(10)	−184.9(7)	29.4(3)
C(35)	7102.4(8)	6958.0(10)	−198.6(6)	23.1(3)
C(36)	7328.3(8)	7777.6(10)	90.4(6)	24.2(3)
Co(1)	1642.6(11)	824.28(12)	2055.25(8)	20.32(6)
C(37)	1551.7(10)	268.9(11)	1291.1(6)	29.2(3)
C(38)	1380.7(9)	−415.4(10)	1756.6(6)	26.2(3)
C(39)	2615.8(9)	1605.7(10)	2053.8(6)	26.4(3)
C(40)	2856.1(9)	656.3(10)	2343.8(6)	25.5(3)
B(1)	−8.5(12)	−336.6(14)	939.5(8)	36.8(4)
B(2)	−218.3(11)	73.1(13)	1574.0(8)	31.3(4)
B(3)	−29.4(12)	823.6(14)	1059.7(9)	37.7(4)
B(4)	740.4(13)	356.2(16)	755.1(8)	39.8(5)

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TABLE 1 (continued)

Atom	x	y	z	U_{equiv}, Å^2
B(5)	1016.7(12)	−681.0(14)	1067.4(8)	36.5(4)
B(6)	435.7(11)	−842.6(12)	1577.0(8)	31.3(4)
B(7)	379.5(11)	1045.2(12)	1784.6(8)	29.2(4)
B(8)	988.4(12)	1207.9(13)	1272.2(8)	32.3(4)
B(9)	676.8(10)	−8.1(11)	2104.9(7)	25.9(3)
B(11)	3382.7(12)	1921.7(14)	3137.2(8)	33.5(4)
B(12)	2936.1(12)	2440.8(13)	2499.2(8)	33.5(4)
B(13)	3550.5(11)	1500.4(14)	2501.7(8)	31.7(4)
B(14)	3352.7(11)	768.7(13)	3012.3(7)	31.1(4)
B(15)	2616.1(11)	1263.1(13)	3340.4(7)	31.7(4)
B(16)	2359.0(12)	2311.4(13)	3021.7(8)	33.5(4)
B(17)	2304.7(10)	429.9(12)	2834.0(7)	27.1(3)
B(18)	1673.0(11)	1391.1(12)	2842.8(7)	28.0(4)
B(19)	1875.5(11)	2129.2(11)	2314.0(8)	29.3(4)
Co(2)	4560.36(11)	8233.98(12)	775.06(8)	20.76(6)
C(41)	3915.6(9)	8556.4(10)	41.0(6)	26.1(3)
C(42)	4772.2(9)	8114.4(10)	−26.8(6)	25.7(3)
C(43)	5454.2(9)	7914.8(10)	1479.8(6)	27.5(3)
C(44)	4595.3(10)	8276.1(10)	1591.5(6)	27.5(3)
B(21)	3534.0(11)	7035.1(12)	−575.4(8)	28.5(4)
B(22)	3968.7(12)	8096.4(12)	−591.2(8)	30.8(4)
B(23)	3104.6(11)	7956.3(13)	−294.7(8)	32.3(4)
B(24)	3202.6(11)	6931.6(12)	61.4(8)	28.9(4)
B(25)	4138.4(11)	6440.9(11)	−10.7(7)	26.3(3)
B(26)	4604.2(11)	7169.7(12)	−412.3(7)	27.9(4)
B(27)	4941.6(10)	7141.0(11)	326.7(7)	24.8(3)
B(28)	4069.7(11)	6978.8(11)	624.4(7)	25.8(3)
B(29)	3430.7(10)	7922.5(12)	445.8(8)	27.2(4)
B(31)	5795.2(13)	9408.1(13)	2129.1(8)	35.1(4)
B(32)	6247.3(12)	8552.2(13)	1799.5(8)	34.0(4)
B(33)	5433.4(13)	8312.3(13)	2131.2(8)	34.7(4)
B(34)	4731.4(13)	9193.1(13)	2002.2(8)	34.4(4)
B(35)	5121.4(12)	9998.2(12)	1598.8(8)	31.9(4)
B(36)	6064.7(11)	9598.7(12)	1474.0(8)	32.5(4)
B(37)	5856.8(11)	8620.3(12)	1068.9(8)	28.4(4)
B(38)	5163.5(11)	9528.1(11)	939.1(7)	27.7(4)
B(39)	4340.9(11)	9260.0(11)	1268.5(8)	27.9(4)

TABLE 2

Basic interatomic distances in $[\text{Mn}^{\text{II}}(1,10\text{-}C_{12}H_8N_2)_3]^{2+}[\text{Co}^{\text{III}}(\pi\text{-}1,2\text{-}C_2B_9H_{11})_2]_2^-$, Å

Bond	Length	Bond	Length
Mn(1)−N(3)	2.2225(13)	Mn(1)−N(6)	2.2348(13)
Mn(1)−N(1)	2.2569(13)	Mn(1)−N(2)	2.2646(12)
Mn(1)−N(4)	2.2709(13)	Mn(1)−N(5)	2.2780(13)
N(1)−C(1)	1.331(2)	N(1)−C(12)	1.362(2)
N(2)−C(10)	1.329(2)	N(2)−C(11)	1.363(2)
C(1)−C(2)	1.397(2)	C(2)−C(3)	1.360(3)
C(3)−C(4)	1.405(3)	C(4)−C(12)	1.410(2)
C(4)−C(5)	1.432(3)	C(5)−C(6)	1.342(3)
C(6)−C(7)	1.432(3)	C(7)−C(8)	1.405(3)
C(7)−C(11)	1.408(2)	C(8)−C(9)	1.367(3)
C(9)−C(10)	1.399(2)	C(11)−C(12)	1.442(2)
N(3)−C(13)	1.328(2)	N(3)−C(24)	1.361(2)
N(4)−C(22)	1.330(2)	N(4)−C(23)	1.363(2)
C(13)−C(14)	1.396(2)	C(14)−C(15)	1.368(2)
C(15)−C(16)	1.408(2)	C(16)−C(24)	1.407(2)

TABLE 2 (continued)

Bond	Length	Bond	Length
C(16)−C(17)	1.433(2)	C(17)−C(18)	1.348(3)
C(18)−C(19)	1.431(2)	C(19)−C(23)	1.408(2)
C(19)−C(20)	1.412(2)	C(20)−C(21)	1.366(3)
C(21)−C(22)	1.398(2)	C(23)−C(24)	1.442(2)
N(5)−C(25)	1.331(2)	N(5)−C(36)	1.362(2)
N(6)−C(34)	1.327(2)	N(6)−C(35)	1.364(2)
C(25)−C(26)	1.399(2)	C(26)−C(27)	1.356(3)
C(27)−C(28)	1.411(2)	C(28)−C(36)	1.410(2)
C(28)−C(29)	1.431(2)	C(29)−C(30)	1.343(3)
C(30)−C(31)	1.430(2)	C(31)−C(35)	1.407(2)
C(31)−C(32)	1.409(2)	C(32)−C(33)	1.368(3)
C(33)−C(34)	1.396(2)	C(35)−C(36)	1.442(2)
Co(1)−C(39)	2.019(2)	Co(1)−C(40)	2.031(2)
Co(1)−C(38)	2.031(2)	Co(1)−C(37)	2.038(2)
Co(1)−B(9)	2.078(2)	Co(1)−B(19)	2.088(2)
Co(1)−B(8)	2.093(2)	Co(1)−B(17)	2.094(2)
Co(1)−B(18)	2.112(2)	Co(1)−B(7)	2.114(2)
C(37)−C(38)	1.615(2)	C(37)−B(4)	1.694(2)
C(37)−B(8)	1.703(2)	C(37)−B(5)	1.724(2)
C(38)−B(6)	1.686(2)	C(38)−B(9)	1.713(2)
C(38)−B(5)	1.728(2)	C(39)−C(40)	1.618(2)
C(39)−B(12)	1.687(2)	C(39)−B(19)	1.708(2)
C(39)−B(13)	1.728(2)	C(40)−B(14)	1.692(2)
C(40)−B(17)	1.702(2)	C(40)−B(13)	1.720(2)
B(1)−B(5)	1.764(3)	B(1)−B(6)	1.767(3)
B(1)−B(4)	1.768(3)	B(1)−B(3)	1.783(3)
B(1)−B(2)	1.783(3)	B(2)−B(6)	1.768(3)
B(2)−B(3)	1.779(3)	B(2)−B(9)	1.780(2)
B(2)−B(7)	1.797(3)	B(3)−B(4)	1.772(3)
B(3)−B(8)	1.779(3)	B(3)−B(7)	1.806(3)
B(4)−B(5)	1.768(3)	B(4)−B(8)	1.799(3)
B(5)−B(6)	1.760(3)	B(6)−B(9)	1.798(2)
B(7)−B(8)	1.799(3)	B(7)−B(9)	1.803(3)
B(11)−B(13)	1.766(3)	B(11)−B(14)	1.772(3)
B(11)−B(12)	1.777(3)	B(11)−B(15)	1.781(3)
B(11)−B(16)	1.784(3)	B(12)−B(13)	1.758(3)
B(12)−B(16)	1.776(3)	B(12)−B(19)	1.807(3)
B(13)−B(14)	1.759(3)	B(14)−B(15)	1.778(3)
B(14)−B(17)	1.798(2)	B(15)−B(17)	1.775(3)
B(15)−B(16)	1.784(3)	B(15)−B(18)	1.800(3)
B(16)−B(19)	1.784(3)	B(16)−B(18)	1.804(3)
B(17)−B(18)	1.804(3)	B(18)−B(19)	1.801(3)
Co(2)−C(43)	2.023(2)	Co(2)−C(41)	2.025(2)
Co(2)−C(44)	2.033(2)	Co(2)−C(42)	2.035(2)
Co(2)−B(37)	2.089(2)	Co(2)−B(29)	2.094(2)
Co(2)−B(27)	2.103(2)	Co(2)−B(39)	2.103(2)
Co(2)−B(28)	2.133(2)	Co(2)−B(38)	2.145(2)
C(41)−C(42)	1.627(2)	C(41)−B(23)	1.702(2)
C(41)−B(29)	1.708(2)	C(41)−B(22)	1.725(2)
C(42)−B(27)	1.705(2)	C(42)−B(26)	1.708(2)
C(42)−B(22)	1.724(2)	C(43)−C(44)	1.619(2)
C(43)−B(32)	1.700(2)	C(43)−B(37)	1.705(2)
C(43)−B(33)	1.721(2)	C(44)−B(39)	1.701(2)
C(44)−B(34)	1.705(2)	C(44)−B(33)	1.724(3)
B(21)−B(22)	1.769(3)	B(21)−B(26)	1.770(2)
B(21)−B(23)	1.775(3)	B(21)−B(24)	1.777(3)
B(21)−B(25)	1.785(3)	B(22)−B(26)	1.763(3)
B(22)−B(23)	1.768(3)	B(23)−B(24)	1.773(3)
B(23)−B(29)	1.792(3)	B(24)−B(29)	1.773(2)
B(24)−B(25)	1.781(2)	B(24)−B(28)	1.791(3)

TABLE 2 (continued)

Bond	Length	Bond	Length
B(25)−B(26)	1.769(2)	B(25)−B(27)	1.780(2)
B(25)−B(28)	1.788(2)	B(26)−B(27)	1.790(2)
B(27)−B(28)	1.786(2)	B(28)−B(29)	1.786(2)
B(31)−B(33)	1.767(3)	B(31)−B(34)	1.779(3)
B(31)−B(35)	1.781(3)	B(31)−B(32)	1.781(3)
B(31)−B(36)	1.787(3)	B(32)−B(33)	1.770(3)
B(32)−B(36)	1.773(3)	B(32)−B(37)	1.785(3)
B(33)−B(34)	1.765(3)	B(34)−B(35)	1.781(3)
B(34)−B(39)	1.792(3)	B(35)−B(36)	1.781(3)
B(35)−B(39)	1.785(3)	B(35)−B(38)	1.788(3)
B(36)−B(37)	1.780(3)	B(36)−B(38)	1.791(3)
B(37)−B(38)	1.787(3)	B(38)−B(39)	1.788(3)

[7]. These are typical for high-spin Mn(II) [8−11]. Bond angles N—Mn—N in five-membered chelate cycles MnN$_2$C$_2$ also are varied in the narrow range of 74.02(5)−74.44(5)^o, mean 74.25(5)^o. The rest valence angles at Mn fall within the ranges of 89.44(5)−104.09 and 160.18(5)−164.97(5)^o which is quite reasonable for a distorted octahedron. Mn atom deviates from mean square planes of Phen molecules by 0.107, 0.146 and 0.119 Å. Metal cycles are bent by close angles (3.2, 4.5 and 4.7^o) in all the three cycles. In plain Phen molecules (least squares deviation being below 0.022 Å), atoms most deviating from the ring planes are N(2) − by 0.047, C(27) by 0.041 and C(29) by 0.043 Å. Bond lengths and valence angles of Phen molecules are usual. The angles between mean square plains of Phen rings are within the range 95.1−104.3^o.

The anions are two icosahedra connected with each other by a common vertex which is occupied by Co(III) atom. As a result, two
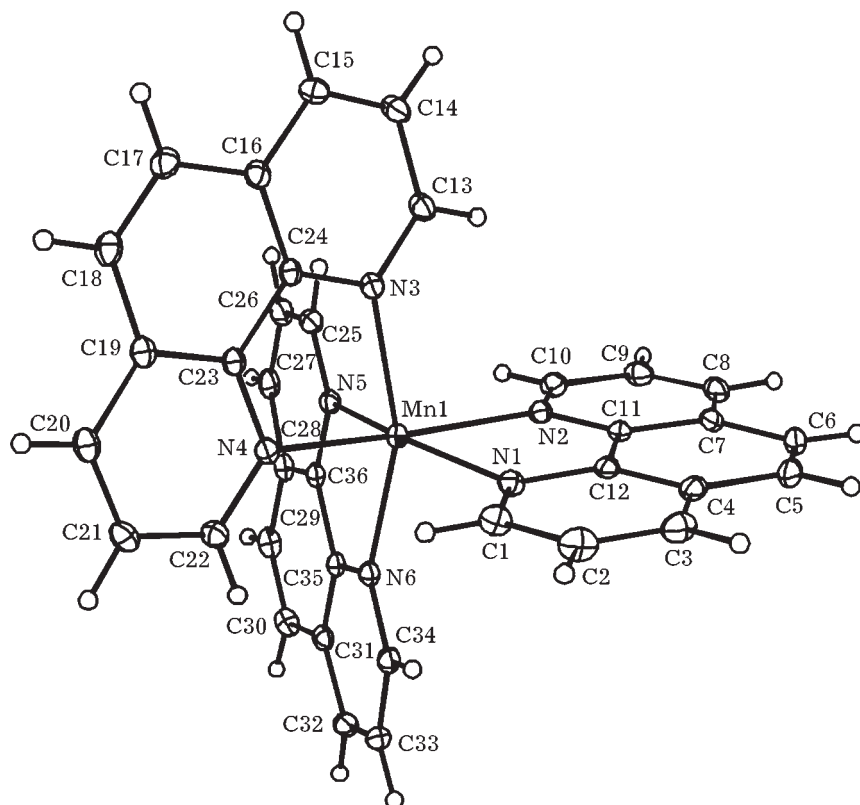

Fig. 1. The structure of Mn(Phen)$_3^{2+}$ cation with numbered atoms and the ellipsoids of heat vibrations of atoms other than hydrogen. H atoms are shown as circles of arbitrary radiis.
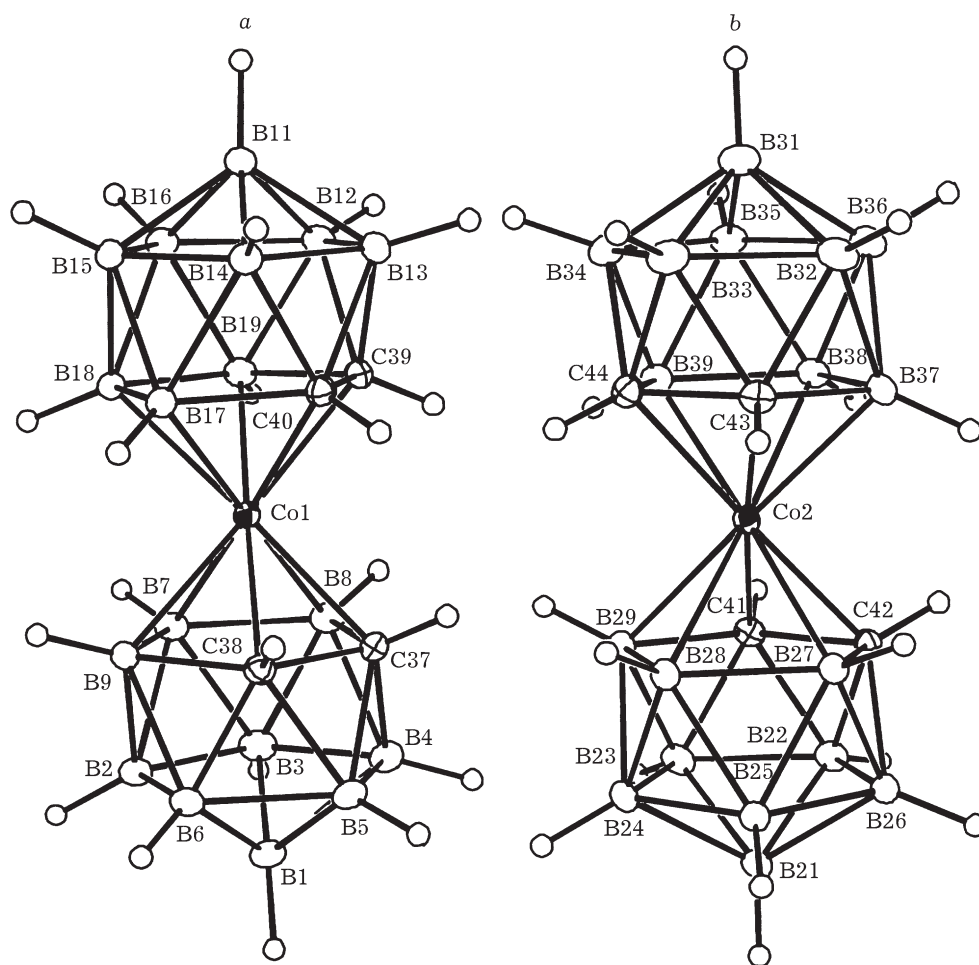
Fig. 2. The structure of the anions $[(C_2B_9H_{11})_2Co(1)]^-$ (*a*) and $[(C_2B_9H_{11})_2Co(2)]^-$ (*b*) with numbered atoms and the ellipsoids of heat vibrations of the atoms other than hydrogen. H atoms are shown as circles of arbitrary radii.

planes $\{C_2B_3\}$ in the anions are bound to Co atom as a η^5 type and have different conformations. For Co(1), the conformation is braked and icosahedral C atoms are not completely cisoid; $C(37)-C(38)$ and $C(39) - C(40)$ vectors possess gauche-configuration; for Co(2), the conformation is less usual, screened, with the transoid positions of cluster C atoms.

Mean square planes determined by the two leagating faces are nearly parallel; the inclination to each other is only $1.1°$ for Co(1) and $0.9°$ for Co(2). Co atoms are at the distances of 1.460 and 1.457 Å (Co(1)), 1.474 and 1.477 Å (Co(2)) from the planes. Transoid position of C—C in the anion with Co(2) leads to larger distance between metal atom and leagating planes. Five leagating planes are not exactly complanar: the faces are bent with respect to B(8)...B(9), B(17)...B(19) near Co(1); B(27)...B(29),

B(37)...(39) near Co(2) and exhibit conformation as an envelope with dihedral angles of 2.7, 2.5, 2.4 and 2.9°, respectively. In the lower pentagonal belts B(2)-B(3)-B(4)-B(5)-B(6), B(12)-B(13)-B(14)-B(15)-B(16), B(22)-B(23)-B(24)-B(25)-B(26), and B(32)-B(33)-B(34)-B(35)-B(36), the complanarity is better and the conformation of the envelope is characterized by smaller angles: 1.4, 1.0, 0.7 and 1.2°. Maximum deviations from mean square planes $\{C_2B_3\}$ are 0.019 Å for B(7), 0.018 Å for B(18), 0.017 Å for B(28) and 0.20 Å for B(38).

The distances from Co atoms to the coordinated carbon atoms of carborane ligands fall within the range 2.019(2)−2.038(2) for Co(1) and 2.023(2)−2.035(2) Å for Co(2), the mean being 2.029(2) E. Similar distances to boron atoms are within the range 2.078(2)−2.114(2) for Co(1) and 2.089(2)−2.145(2) Å for Co(2), with a mean of
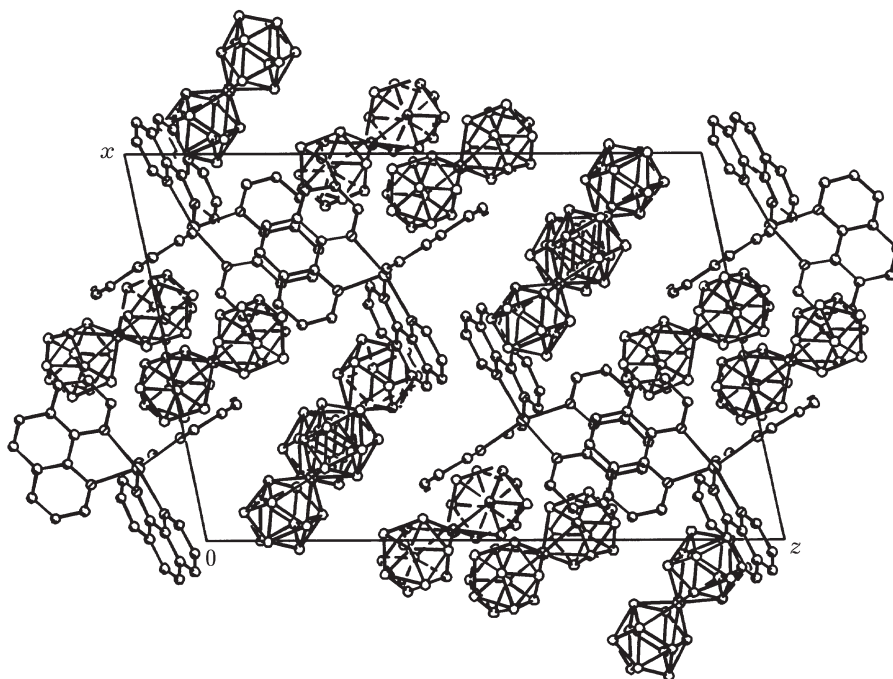
Fig. 3. The projection of the crystal structure on the (010) plane. H atoms are omitted for simplicity.

2.104(2) Å. Cluster C atoms are located at C—C distances of $1.615(2) - 1.627(2)$ Å, with a mean of 1.620(2) Å. Cluster distances B—B and C—B are within the ranges $1.758(3)-1.807(3)$ and $1.686(2)-1.728(2)$ with the mean 1.781(3) and 1.709(2) Å, respectively. These figures are in good agreement with similar distances in similar compounds reported earlier [2, 3, 12, 13]. B—H and C—H distances are within the ranges $1.04(2)-1.12(2)$ and $0.92(2)-0.98(2)$ with mean 1.08(2) and 0.95(2) Å.

Figure 3 shows the projection of the crystal structure on the (010) plane.

CONCLUSION

Low-temperature X-ray structural investigation of **1** showed that the $Mn(Phen)_3^{2+}$ cation is able of forming two conformations of the anion $[Co(C_2B_9H_{11})2]$ corresponding to a single formula unit. This fact confirms the possibility of the effect of cation component on the conformational structure of the "sandwich" complex of Co(III) bisdicarbollide.

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