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Instrumental Achievements

Crystal Structure of Bis{(*N,N′*-dimethylformamide)(μ-formato)[μ-bis-(salicylidene)-1,3-propanediaminato]nickel(II)}cobalt(II)monohydrate

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Trinuclear linear homo or heteronuclear complexes based on Schiff-base ligands are of interest because of their magnetic super-exchange interactions between bridged metal ions.[1,2] The synthesis and structural properties of trinuclear linear complexes have been the subject of considerable interest in our laboratories.[3,4] We describe here a new heterometallic trinuclear complex, $[Co\{(CO_2H)(SALPD)Ni(DMF)\}_2 \cdot H_2O]$.

To a solution of *N,N′*-bis(salicylidene)-1,3-propanediamine (1.410 g, 5 mmol) in EtOH (50 ml), an ammonia solution (%20, 10 ml) was added, and the mixture was heated to the boiling point. Then, a solution of $NiCl_2 \cdot 6H_2O$ (1.185 g, 5 mmol) in hot water was added, and the final mixture was set aside. After 2 h, light-green Ni crystals were filtered and dried in an oven at 423 – 433 K. This complex (0.338 g, 1 mmol) was dissolved in hot DMF (50 ml) and the temperature of the solution was increased to the boiling point. A solution of $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol) in hot MeOH (20 ml) and a solution of NaHCOO (0.068 g, 1 mmol) in hot water (5 ml) were added to this solution. The resulting mixture was set aside for three days, and the light-brown crystals which formed were filtered off and dried in air. A chemical diagram of the title compound is shown in Fig. 1.

The structure consists of a linear heterotrinuclear unit with a central Co^{II} ion. The coordination around cobalt is a distorted octahedron involving four bridging O atoms from two $SALPD^{2-}$ (*N,N′*-bis(salicylidene)-1,3-propanediamine) ligands in the equatorial plane and an O atom from each of the two bridging formate groups (Fig. 2). The two inversion-related Ni^{II} ions are coordinated by the two O and two N atoms from the $SALPD^{2-}$ ligand. The coordination sphere is completed by the O atom of the bridging formate on one side and by a dmf (dimethylformamide) ligand O atom on the other.

The coordination observed in bis{(*N,N′*-dimethylformamide)(μ-formato)[μ-bis(salicylidene)-1,3-propanediaminato]nickel(II)}cobalt(II)monohydrate is similar to that reported by bis[μ-*N,N′*-bis(salicylidene)-1,3-propane-diaminato]-(dimethylformamide)-(μ-nitrito-N)nickel(II)]cobalt(II).[1] Similar bond distances and angles were observed for both trinuclear

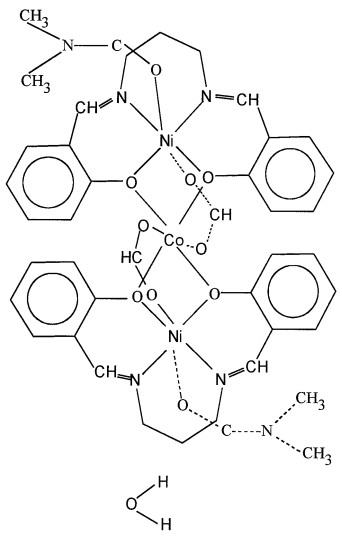

Fig. 1 Chemical diagram.

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Table 1 Crystal and experimental data

Formula: $C_{42}H_{48}CoN_6Ni_2O_{11}$	
Formula weight = 989.20	
Space group: $P2_1/c$	
Crystal system: monoclinic	$Z = 2$
a = 10.5517(11)Å	
b = 16.6399(12)Å	
c = 13.8251(13)Å	
β = 111.135(3)°	
V = 2264.1(3)Å^3	
D_x = 1.428 g/cm^3	
μ(Mo K$_\alpha$) = 1.246 mm^{-1}	
T = 295 K	
Color = light brown	
Radiation Mo K$_\alpha$ (λ = 0.71073 Å)	
0.20 × 0.15 × 0.10	
$2\theta_{max}$ = 49.6°	
No. of reflection = 4120	
No. of reflection used = 3896($I > 2\sigma(I)$)	
No. of parameters = 278	
R_1 = 0.05	
wR_2 = 0.15	
Goodness-of-fit = 0.96	
$(\Delta\rho)_{max}$ = 0.92 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.88 eÅ^{-3}	
Measurement: Enraf-Nonius CAD-4	
Program system: SHELX97	
Structure determination: SHELXS97	
Refinement: full matrix least-squares SHELXL97	
Treatment of hydrogen atoms: geometric calculation	

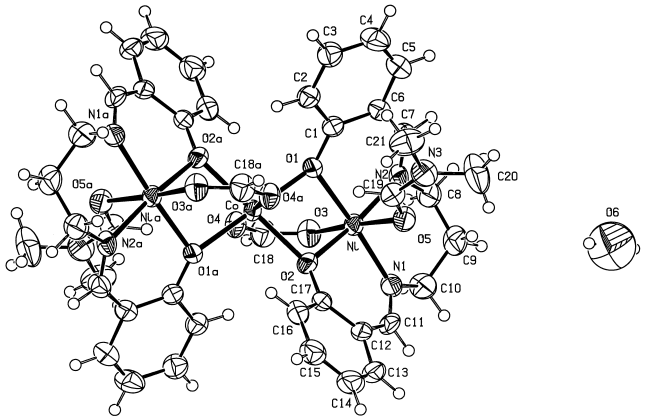

Fig. 2 Molecular structure of the title compound with the atom numbering scheme. H atoms are shown as small circles with arbitrary radii.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}
Co	0.5000	0.5000	0.5000	2.50(4)
Ni	0.26494(9)	0.38474(5)	0.38892(7)	2.72(3)
N1	0.0727(6)	0.3800(4)	0.3859(5)	3.24(6)
N2	0.2426(6)	0.3008(4)	0.2777(5)	3.08(5)
N3	0.4647(7)	0.1984(4)	0.5945(5)	4.17(9)
O1	0.4650(5)	0.3939(3)	0.4090(4)	2.75(5)
O2	0.3171(5)	0.4612(3)	0.5098(4)	2.87(5)
O3	0.2124(5)	0.4783(3)	0.2810(4)	3.75(4)
O4	0.3837(5)	0.5627(3)	0.3668(4)	3.29(4)
O5	0.3028(5)	0.2847(3)	0.4971(4)	3.55(5)
O6*	0.0000	0.5000	0.0000	13.1(5)
C1	0.5387(7)	0.3307(4)	0.4062(5)	2.83(5)
C2	0.6798(7)	0.3313(5)	0.4615(6)	3.25(6)
C3	0.7582(8)	0.2648(5)	0.4627(6)	3.86(3)
C4	0.7015(9)	0.1958(5)	0.4093(7)	4.73(6)
C5	0.5647(9)	0.1950(5)	0.3516(7)	4.33(6)
C6	0.4806(8)	0.2604(5)	0.3483(6)	3.28(7)
C7	0.3383(8)	0.2549(5)	0.2803(6)	3.57(7)
C8	0.1083(8)	0.2851(5)	0.2010(7)	4.34(5)
C9	0.0038(8)	0.2747(5)	0.2507(7)	4.50(5)
C10	-0.0364(8)	0.3518(5)	0.2933(7)	4.26(5)
C11	0.0413(7)	0.3992(4)	0.4630(7)	3.47(5)
C12	0.1323(7)	0.4273(4)	0.5639(6)	3.16(7)
C13	0.0813(9)	0.4272(5)	0.6443(7)	3.94(5)
C14	0.1590(11)	0.4506(5)	0.7431(8)	4.80(6)
C15	0.2900(10)	0.4774(5)	0.7636(7)	4.34(5)
C16	0.3429(9)	0.4819(4)	0.6851(6)	3.55(4)
C17	0.2652(7)	0.4570(4)	0.5835(6)	2.72(4)
C18	0.2769(9)	0.5430(5)	0.2950(7)	4.02(4)
C19	0.4212(8)	0.2697(5)	0.5580(6)	3.20(7)
C20	0.3803(12)	0.1272(5)	0.5653(10)	7.09(7)
C21	0.6085(9)	0.1861(7)	0.6591(7)	5.36(7)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.
*This atom refined isotropically and the multiplicity are 0.5.

Table 3 Selected bond distances (Å) and angles (°)

Co	O1	2.122(4)	Ni	O1	2.033(5)
Co	O2	2.085(5)	Ni	O2	2.012(5)
Co	O4	2.086(5)	Ni	O3	2.089(5)
Ni	N1	2.015(6)	Ni	O5	2.176(5)
Ni	N2	2.028(6)			
O2	Ni N1	90.8(2)	O2	Ni N2	170.9(2)
N1	Ni N2	96.7(3)	O2	Ni O1	83.10(19)
N1	Ni O1	173.5(2)	N2	Ni O1	89.2(2)
O2	Ni O3	92.6(2)	N1	Ni O3	90.5(2)
N2	Ni O3	92.5(2)	O1	Ni O3	92.1(2)
O2	Ni O5	89.1(2)	N1	Ni O5	85.3(2)
N2	Ni O5	86.4(2)	O1	Ni O5	92.25(19)
O3	Ni O5	175.5(2)	C1	O1 Ni	122.1(4)
C1	O1 Co	134.7(4)	Ni	O1 Co	95.34(19)

complexes. The Co··Ni distances for both complexes are 3.0727(6) (this work) and 2.9881(11)Å. In the Co^{II} coordination sphere, the Co–O($SALPD^{2-}$) bond lengths between (2.085(5) – 2.122(4)) and Co–O(formate) is 2.086(5)Å. The Ni–O bond lengths are in the range of (2.012(5) – 2.176(5))Å, and the longest distance is Ni–O(dmf). The Ni–N1 and Ni–N2 bond lengths are 2.015(6) and 2.028(6)Å, respectively. The Ni–O–Co, O–Ni–O, N–Ni–N bond angles for both complexes are [95.34(19), (89.1(2) – 175.5(2)), 96.7(3)° (this work)] and [93.9(2), (82.1(2) – 91.2(2)), 97.6(3)°], respectively.

The title compound has an extra lattice water molecule in the structure and the nearest distance between water and moiety O6–C8 is 4.419(6)Å.

The crystal and experimental data are given in Table 1. The final atomic parameters are presented in Table 2. Selected bond distances and angles are given in Table 3.

Acknowledgements

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