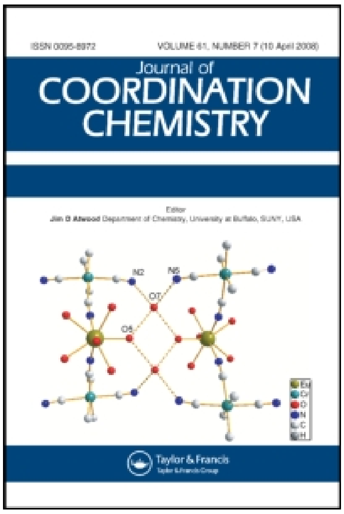

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and thermoanalysis of bis{[μ-bis-*N*,*N*′-(2-hydroxybenzoyl)-1,3-propandiaminato](*N*,*N*′-dimethyl formamide) (μ-benzoato)nickel(II)}nickel(II)

Abdülkadir Akay[a]; Cengiz Arici[b]; Orhan Atakol[a]; Hartmut Fuess[c]; Ingrid Svoboda[c]
[a] Department of Chemistry, University of Ankara, Tandoğan - Ankara, 06100, Turkey [b] Department of Engineering Physics, University of Hacettepe, Beytepe - Ankara, 06532, Turkey [c] Strukturforschung, FB Materialwissenschaft, Technische Universitat Darmstadt, Darmstadt, Germany

To cite this Article Akay, Abdülkadir , Arici, Cengiz , Atakol, Orhan , Fuess, Hartmut and Svoboda, Ingrid(2006) 'Synthesis, crystal structure and thermoanalysis of bis{[μ-bis-*N*,*N*′-(2-hydroxybenzoyl)-1,3-propandiaminato](*N*,*N*′-dimethyl formamide) (μ-benzoato)nickel(II)}nickel(II)', Journal of Coordination Chemistry, 59: 8, 933 — 938

To link to this Article: DOI: 10.1080/00958970500410374

URL: http://dx.doi.org/10.1080/00958970500410374

Journal of Coordination Chemistry
Vol. 59, No. 8, 20 May 2006, 933–938

Synthesis, crystal structure and thermoanalysis of bis{[μ-bis-*N*,*N*′-(2-hydroxybenzoyl)-1,3-propandiaminato](*N*,*N*′-dimethyl formamide)(μ-benzoato)nickel(II)}nickel(II)

ABDÜLKADIR AKAY†, CENGIZ ARICI*‡,
ORHAN ATAKOL†, HARTMUT FUESS§ and INGRID SVOBODA§

†Department of Chemistry, University of Ankara,
Tandoğan – Ankara, 06100, Turkey
‡Department of Engineering Physics, University of Hacettepe,
Beytepe – Ankara, 06532, Turkey
§Strukturforschung, FB Materialwissenschaft, Technische Universitat Darmstadt,
Petersen Strasse, 23 D-64287, Darmstadt, Germany

(*Received in final form 18 August 2005*)

The title compound is a centrosymmetric, linear, homotrinuclear nickel(II) complex and has been characterized by elemental and thermogravimetric analysis, IR spectroscopy and single-crystal X-ray diffraction. The complex is monoclinic, space group $P2_1/n$, with $a = 13.707(4)$, $b = 13.455(2)$, $c = 14.620(3)\,Å$, $\beta = 101.300(2)°$, $V = 2644.1(10)\,Å^3$ and $Z = 2$. The central and terminal nickel(II) ions have distorted octahedral geometry with a Ni $\cdots$ Ni distance of 3.047(1) Å.

Keywords: Homotrinuclear complex; Nickel(II); Reduced Schiff base; Thermogravimetric analysis; Crystal structure

1. Introduction

Trinuclear, linear, homo- or heteronuclear complexes based on Schiff base ligands are of interest because of magnetic superexchange interactions between bridged metal ions [1]. In these complexes, various combinations of metal ions in the central and terminal locations, and μ-bridges, such as acetate, formate, nitrate and nitrite anions, are possible [2–5]. Bis-*N*,*N*′(salicylidene)1,3-propanediamine is a long-known Schiff base and trinuclear complex formation with it has been studied [1]. Schiff bases can be reduced to amines very easily by $NaBH_4$ [6]. In this study, Bis-*N*,*N*′(salicylidene)-1,3-propanediamine was reduced to the amine form using $NaBH_4$ in MeOH and trinuclear complex

---

*Corresponding author. Email: arici@hacettepe.edu.tr

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500410374

formation examined. Benzoate has been used as bridging ligand [7]. The structure of a complex obtained was investigated using elemental and thermogravimetric analysis, IR spectroscopy and X-ray diffraction techniques.

2. Experimental

C, H, N analyses were carried out with a Leco 932 instrument. Ni analysis was performed using a Hitachi 8200 D atomic absorption spectrometer. IR spectra (KBr disks) were recorded on a Mattson FTIR 1000 spectrophotometer.

2.1. *Preparation of the ligand*

N,*N′*(salicylidene)-1,3-propanediamine was reduced using excess $NaBH_4$ in MeOH. The reduced form was isolated from MeOH by addition of H_2O.

2.2. *Preparation of the complex*

The ligand was dissolved in hot DMF. To this solution was added a hot MeOH solution of $NiCl_2 \cdot 6H_2O$, the ligand/Ni(II) ratio being 3/2, and a hot aqueous solution of sodium benzoate equivalent in amount to Ni(II). The mixture was left to stand for 3 days and the resulting crystals filtered off and dried in air. Anal. Calcd for $C_{54}H_{64}N_6O_{10}Ni_3$ (%): C, 57.23; H, 5.63; N, 7.41; Ni, 15.54. Found: C, 57.48; H, 4.97; N, 7.56; Ni, 15.83. IR (cm^{-1}): $\nu_{N\text{–}H}$ 3257, $\nu_{C\text{–}H(Ar)}$ 3055–3020, $\nu_{C\text{–}H(Aliph)}$ 2922–2853, $\nu_{C=O(DMF)}$ 1646, $\nu_{C=C(Ar)}$ 1598, δ_{CH2} 1483, $\delta_{C\text{–}H(Ar)}$ 756–7255.

2.3. *Thermal analysis*

Thermogravimetric analysis was performed with Shimadzu DTG 60H and DSC 60 instruments. DTA and TGA thermograms were obtained between room temperature and 750°C under nitrogen with a heating rate of 10–30°C min^{-1}. DSC was measured over the range 30–480°C.

2.4. *X-ray crystallography*

X-ray intensity data were collected at room temperature using an Enraf-Nonius CAD 4 diffractometer [12] with Mo-Kα radiation using the $\omega/2\theta$ scan mode. Cell parameters were determined from least-squares refinement of 25 centred reflections in the range $1.86 \leq \theta \leq 25.98°$. Three standard reflections were measured every 120 min during data collection and showed no significant intensity variation. Some 5184 unique reflections were measured, of which 4039 had $I \geq 2\sigma(I)$ and these were used for structure determination and refinement. Cell refinement and data reduction were carried out using SHELXL97 [13]. The structure was solved by direct methods using SHELXS97 [13] in the WinGX package [14]. All non-hydrogen atoms were refined isotropically and then anisotropically by full-matrix least-squares based on F^2. All hydrogen atoms were placed geometrically and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The final cycle of refinement included 331 variable parameters and gave $R = 0.0329$, $wR = 0.0894$, goodness-of-fit = 1.04. The minimum and maximum residual electron densities were −0.327 and 0.415 e Å^{-3}, respectively. A PLATON drawing [15] of the molecule with 50% probability thermal ellipsoids and showing the atom numbering scheme is shown in figure 1. Crystal and refinement data are given in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

As can be seen in figure 1, the three Ni(II) ions have octahedral coordination spheres with three octahedra situated side by side. Terminal and central Ni(II) ions are situated in N_2O_4 and O_6 spheres, respectively, and phenolic oxygen atoms coordinate both. In the terminal Ni(II) ions, two phenolic oxygen and two amine nitrogens of the ligand form the basal plane. An oxygen atom of to DMF and a benzoate oxygen atom occupy apical positions. A similar complex has been prepared previously [7]. The only difference in this complex is the μ-bridge (benzoate) combining the central and terminal Ni(II) ions. The Ni $\cdots$ Ni distance is 3.047(1) Å. The Ni2–N1–C9–C10–C11–N2 chelate ring formed between the organic ligand and

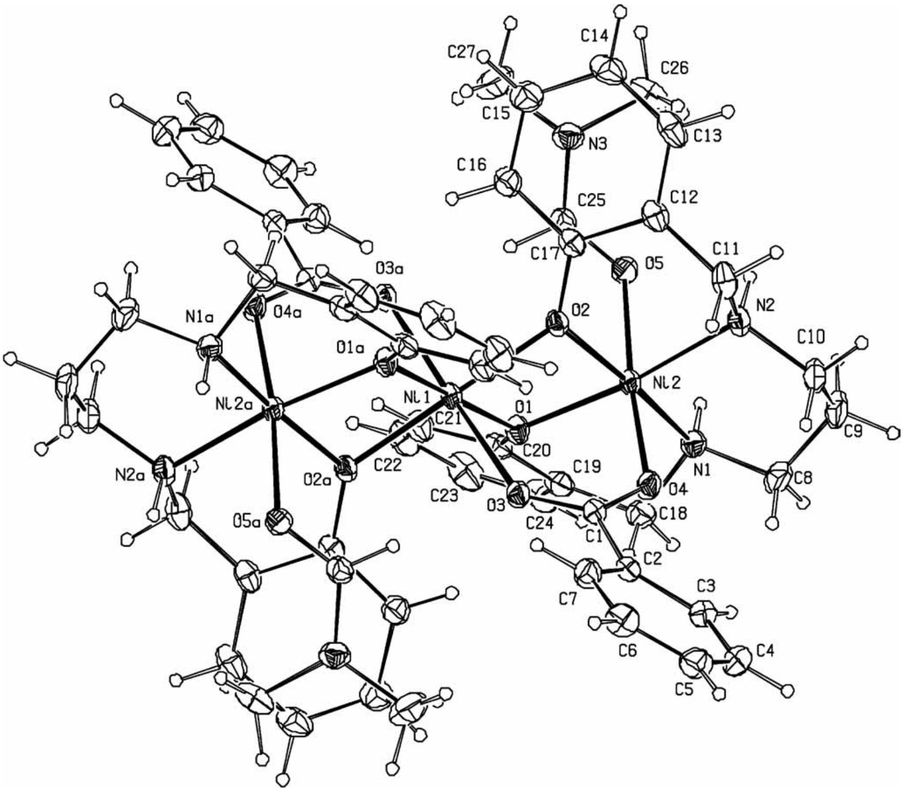

Figure 1. PLATON drawing of the complex with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Crystal data and refinement details for the complex.

Empirical formula	$C_{54}H_{64}N_6Ni_3O_{10}$
Formula weight	1133.24
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions (Å, °)	
a	13.707(4)
b	13.455(2)
c	14.620(3)
β	101.300(2)
V (Å^3)	2644.1(10)
Z	2
D_c (g cm^{-3})	1.423
μ (mm^{-1})	1.121
$F(000)$	1188
Crystal size (mm^3)	$0.35 \times 0.30 \times 0.25$
θ_{max} (°)	25.98
Index range	$-16 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 18$
Number of reflections	5184
Number of parameters	331
R_{int}	0.032
R	0.0329
wR	0.0894
Goodness-of-fit	1.04
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.327, 0.415

the terminal Ni(II) ion adopts a distorted chair conformation as expected. The C9 atom distance from the N1–C8–C10–N2 plane is 0.712(4) Å, whereas the Ni2 distance is −0.869(1) Å. Two intramolecular hydrogen bond exist in the molecule between the iminic nitrogen (N1,N2) and DMF oxygen (O5) atoms. DHA angles are 102.57(3) and 103.86(3)° and H ··· D and D ··· H distances are normal.

3.2. *Thermal analysis*

Upon heating, coordinated DMF molecules are lost first at 200–280°C (Calcd 12.96, found 12.7%). The second mass loss of 33.3% concerns ligand and benzoate degradation with possible formation of the benzophenone. A carbonyl compound is formed with thermal degradation of metal acetates [8]. The total theoretical mass loss corresponding to benzophenone and the aliphatic groups around terminal Ni(II) is 33.2%. The degradation mechanism cannot be totally explained, although recent papers dealing with ONNO type ligands report similar mass losses [2–5]. Nickel phenolate and $NiCO_3$ are present in the residue at 420°C. Beyond this temperature, and up to 750°C, a slow decrease in mass is observed. This corresponds to degradation of the organic structure and loss of CO_2 from $NiCO_3$; at temperatures higher than 750°C the stoichiometric amount of NiO is almost formed.

Kinetics dealing with loss of DMF molecules in the temperature range 200–270°C and ligand degradation between 280 and 420°C were analyzed using the methods of Horowitz and Metzger [9], Coats and Redfern [10] and Lee [11], and results are summarized in table 3. For the former, ΔH values calculated according to the three methods specified are 163, 183 and 141 kJ mol^{-1}, respectively (mean 158 kJ mol^{-1}). There is little difference between the activation energies (E^*) and accompanying ΔH values calculated according to the three methods, but the frequency factors (Arrhenius con-

Table 2. Selected bond lengths (Å) and bond angles (°) for the complex.

Ni1–Ni2	3.0467(9)
N1–Ni2	2.073(2)
N2–Ni2	2.090(2)
Ni1–O1	2.0323(15)
Ni1–O2	2.0461(16)
Ni1–O3	2.1202(16)
Ni2–O1	2.0217(16)
Ni2–O2	2.0414(16)
Ni2–O4	2.0494(17)
Ni2–O5	2.1485(17)
O1^a–Ni1–O2	98.73(6)
O1–Ni1–O2	81.27(6)
O1^a–Ni1–O3	92.35(6)
O1–Ni1–O3	87.65(6)
O2^a–Ni1–O3	95.29(6)
O2–Ni1–O3	84.71(6)
O1–Ni2–O2	81.64(6)
O1–Ni2–O4	91.38(7)
O2–Ni2–O4	90.20(7)
O1–Ni2–N1	93.06(7)
O2–Ni2–N1	174.20(7)
O4–Ni2–N1	92.27(8)
O1–Ni2–N2	173.15(7)
O2–Ni2–N2	92.30(8)
O4–Ni2–N2	91.85(8)
N1–Ni2–N2	92.85(8)
O1–Ni2–O5	94.89(7)
O2–Ni2–O5	91.08(7)
O4–Ni2–O5	173.72(7)
N1–Ni2–O5	87.02(7)
N2–Ni2–O5	81.96(8)
Ni2–O1–Ni1	97.45(7)
Ni2–O2–Ni1	96.38(7)

[a] Symmetry code: $1-x$, $1-y$, $1-z$.

Table 3. Thermoanalytical and kinetic data for the complex.

	Mass loss (%)		Kinetic parameters (kJ mol^{-1})						
Temp. range	DSC (kJ mol^{-1})	Expected	Found	Method	E^*	A (s^{-1})	ΔH^*	ΔS^*	ΔG^*
206–273	158 ± 11	12.96	12.5	Coats–Redfern	172	2.4×10^{20}	163	140	93
		DMF loss		Horowitz–Metzger	192		183		
				Ozawa	149	2.0×10^{6}	141		
282–420	105 ± 8	33.21	32.7	Coats–Redfern	83	1.2×10^{18}	78	95	26
		Ligand degradation		Horowitz–Metzger	92		87		
				Ozawa	105	4.8×10^{6}	100		

stants) vary in line with the differing calculation methods [16]. The thermal degradation mechanism between 280 and 420°C cannot be clearly explained. In this temperature range, it is probable that the central Ni(II) benzoate is converted to $NiCO_3$ and thermal degradation and evaporation of the organic ligand surrounding the terminal Ni(II) ions occurs. The measured heat of absorption in this temperature range is $105 \pm 8\,\mathrm{kJ\,mol^{-1}}$, whereas theoretically calculated values were 78, 87 and 100 kJ mol^{-1}. Although the agreement is reasonable, the frequency factors are again very different.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279545. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Orhan Atakol is grateful to DAAD for support and wishes to acknowledge the financial support of the Ankara University Research Fund (Project No. 20030705083).

References

[1] C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, M. Mori. *J. Chem. Soc., Dalton Trans.*, 3473 (1990).
[2] O. Atakol, C. Arıcı, M.N. Tahir, R. Kurtaran, D. Ülkü. *Anal. Sci.*, **15**, 933 (1999).
[3] A. Gerli, K.S. Hagen, L.G. Marzilli. *Inorg. Chem.*, **30**, 4673 (1991).
[4] F. Birkelbach, T. Weybermuller, M. Lengen, M. Gerdan, A.F. Trautwein, K. Wieghardt, P. Chaudhuri. *J. Chem. Soc., Dalton Trans.*, 4259 (1997).
[5] F. Ercan, O. Atakol, C. Arıcı, I. Svoboda, H. Fuess. *Acta Cryst.*, **C58**, m193 (2002).
[6] H. Aneetha, K. Pannerselvam, T.-F. Liou, T. Huey-Lu, C. Chung. *J. Chem. Soc., Dalton Trans.*, 2689 (1999).
[7] L.T. Yıldırım, O. Atakol. *Cryst. Res. Technol.*, **12**, 1352 (2002).
[8] T. Arii, A. Kishi, M. Ogawa, Y. Sawada. *Anal. Sci.*, **17**, 875 (2001).
[9] H.H. Horowitz, G. Metzger. *Anal. Chem.*, **35**, 1464 (1963).
[10] A.W. Coats, J.P. Redfern. *Nature*, **201**, 68 (1964).
[11] J.Y. Lee, M.J. Shim, S.W. Kim. *J. Appl. Pol. Sci.*, **81**, 479 (2001).
[12] Enraf-Nonius. Cad-4 Express. Version 1.1, Delft, The Netherlands (1993).
[13] G.M. Sheldrick. *SHELXS97 and SHEXL97. Programs for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).
[14] L.J. Farrugıa. *J. Appl. Cryst.*, **32**, 837 (1999).
[15] A.L. Spek. *PLATON. Program for Crystal Molecular Drawing*, University of Ultrech, The Netherlands (2000).
[16] H. Zhang, B.S. Mitchell. *J. Mater. Res.*, **15**, 1000 (2000).