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Synthesis and Characterization of Cobalt(II), Nickel(II), and Zinc(II) Complexes with N,N'-bis(2-nitrocinnamaldehyde)-1,2-diiminoethane Ligand. Crystal Structure of Zn(nca₂en)Br₂

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Synthesis and Characterization of Cobalt(II), Nickel(II), and Zinc(II) Complexes with N,N'-bis(2-nitrocinnamaldehyde)-1,2-diiminoethane Ligand. Crystal Structure of Zn(nca₂en)Br₂

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A series of complexes of the type $M(nca_2en)X_2$, where $nca_2en = N,N'$ -bis(2-nitrocinnamaldehyde)-1,2-diiminoethane, M(II) = Co, Ni or Zn and X = Cl, Br, I have been synthesized and characterized. The crystal and molecular structure of Zn(nca_2 . en)Br₂ 8 was determined by X-ray crystallography from singlecrystal data. The complex 8 crystallizes in monoclinic system, having Zn ion in distorted tetrahedral geometry, Br(1)-Zn(1)-Br(2), 117.37(4)°; N(3)-Zn(1)-N(2), 82.57(18)°. This structure consists of intermolecular hydrogen bond of the type C-H-X. The formation of the C-H-M weak intramolecular hydrogen bonds due to the trapping of C-H bonds in the vicinity of the metal atoms is reported for 8. The ¹H NMR study of Zn complexes gives further evidence for the presence of such interactions. The spectral properties of the above complexes are also discussed.

Keywords Schiff base complexes, cobalt(II), nickel(II), zinc(II), tetrahedral, crystal structures, nitrocinnamaldehyde

INTRODUCTION

The coordination chemistry of transition metal containing the Schiff base ligands have been of interest for many years.^[1,2] These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures.^[3–6] Bidentate ligands containing imine groups have also been used as the modulators of structural and electronic properties of transition metal centers.^[7] Many MLX₂ complexes of Co(II), Ni(II), and Zn(II) with L = diimine have been investigated. In spite of the diversity in the coordination environment and the structure of these complexes, which depend on the type of Schiff base and the anion, bulky ligands and/or anions will force tetrahedral coordination,^[8-13] here, we have synthesized and characterized a series of M(nca₂en)X₂ complexes with a new bidentate ligand nca₂en (N,N'-bis(2-nitrocinnamalde-hyde)-1,2-diiminoethane) and X = halides (Fig. 1). The crystal structure of Zn(nca₂en)Br₂ complex is presented here.

EXPERIMENTAL

All reagents were used as supplied by Aldrich and Fluka without further purification. Solvents used for the reactions were purified and dried by conventional methods.^[14] NMR spectra were obtained on a Bruker Avance DRX500 (500 MHz) spectrometer. Proton chemical shifts are reported in part per million (ppm) relative to an internal standard of Me₄Si, and the J values are reported in Hertz. The UV-Vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer with quartz cells (1 cm path length). Elemental analyses were performed by using Heraeus CHN-O RAPID elemental analyzer. IR spectra were recorded as KBr pellets on a Shimadzu 435 spectrophotometer. The ligand N,N'-bis(2-nitrocinnamaldehyde)-1,2-diiminoethane, nca2en, Co(nca2en)Cl2 and Ni(nca2en)Br2 was prepared according to previously reported method.^[12,13]

General Procedures for Synthesis of Cobalt Complexes, [Co(nca₂en)X₂]

To a solution of $nca_2en 1 \text{ mmol in } 10 \text{ ml } CH_2Cl_2$ was added 1 mmol of anhydrous CoX_2 , and stirred at room temperature (r.t.) for 3 h under nitrogen atmosphere. The reaction mixture was filtered off. The volume of the solvent was reduced

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FIG. 1. Chemical formula of the complexes 1-9.

under vacuum to about 1 ml. The diffusion of diethyl ether vapor into the concentrated solution gave needle like blue crystals suitable for X-ray studies. The crystals were filtered off and washed with a mixture of diethylether-dichloromethane (9:1 v/v), and dried in vacuo. The spectral data and elemental analysis of complexes are summarized in Table 1.

General Procedures for Synthesis of Nickel Complexes, [Ni(nca₂en)X₂]

To a stirring solution of 1 mmol of anhydrous NiX₂ in 20 ml acetonitrile was added dropwise a solution of 1 mmol nca₂en in 10 ml acetonitrile, and refluxed for 30 min. The solvent was evaporated on a rotatory evaporator at 40°C under reduced pressure. The solid residue was dissolved in 20 ml acetonitrile and filtered off. The filtrate was left overnight under diffusion of diethyl ether to give pink-red crystals. The spectral data and elemental analysis of complexes are summarized in Table 1.

General Procedures for Synthesis of Zinc Complexes, [Zn(nca₂en)X₂]

To a solution of 1 mmol ZnX_2 in 10 ml ethanol was added a solution of 1 mmol nca₂en in 5 ml methanol and stirred at room temperature for 3 h. The product precipitated as a white microcrystalline powder and collected by filtration. The crude product was recrystallized from acetone to give white needleshape crystals. The crystals were collected by filtration and dried in vacuo. The spectral data and elemental analysis of complexes are summarized in Table 1.

Crystal Structure Determination

Suitable single crystal of $[Zn(nca_2en)Br_2]$, was obtained by slow evaporation of an acetone solution of **6** at r.t. Diffraction data for **8** were collected on a STOE-IPDSII diffractometer using graphite-monochromated MoK_{α} radiation $(\lambda = 0.71073 \text{ Å})$. The structure was solved by direct methods (SHELXS-97).^[15] The structure refinement was performed by a full-matrix least-squares method against F^2 (SHELXL-97).^[16] All non-H-atoms were refined anisotropically, all H-atoms were inserted in calculated positions. Crystallographic data (excluding structure factors) for the structure **8** reported in this paper have been deposited with the *Cambridge Crystallographic Data Center*, CCDC No. 616198. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc. cam.ac.uk or (http://www.ccdc.cam.ac.uk)).

RESULTS AND DISCUSSION

N,N'-bis(2-nitrocinnamaldehyde)-1,2-diiminoethane, nca_2en was prepared by the condensation of 2-nitrocinnamaldhyde with ethylenediamine. The product, as a white solid material, was characterized by IR, UV-Vis and ¹H, ¹³C-NMR spectroscopy. The cobalt complexes were prepared by reacting equimolar quantities of the anhydrous cobalt halides salts and nca_2en in dichloromethane. These complexes are stable in air in the solid state. The stability of cobalt complexes in solution depends on the solvent used. The compounds are stable in dichloromethane for at least 24 h, while they are much less stable in methanol. A methanolic solution in open air slowly turns brown in 6 h.

To avoid any oxidation of the cobalt complexes, the synthesis of them were carried out under nitrogen atmosphere. The nickel complexes were prepared by reacting equimolar quantities of the anhydrous nickel halides salts and nca₂en in boiling acetonitrile. The zinc complexes were prepared by reacting equimolar quantities of anhydrous zinc salts and nca₂en in dichloromethane. The zinc complexes are colorless solids dissolving in chloroform, methanol, ethanol and acetone and they are stable at ambient conditions.

IR Spectra

All complexes show similar IR spectral features, exhibiting a strong band between 1629 and 1639 cm⁻¹ corresponding to ν (C=N). This band is shifted to the lower frequencies by 6–20 cm⁻¹ relative to the free ligand upon the coordination of the nitrogen atoms.^[17] The observation of a strong bands at 1350 and 1550 cm⁻¹ in the IR spectrum of complexes assigned to the NO₂ group of ligand in these complexes.^[18]

¹H-NMR Spectra

The ¹H-NMR spectral data of Zn complexes are summarized in Table 1. The ¹H-NMR data of the Zn complexes suggest that the ligand has a symmetrical structure with H₂ and H₃ protons (Fig. 1) in trans positions (J = 9.5 Hz). The four methylene protons appear as a singlet at about 4 ppm. The two vinyl CH protons (H₃) are observed as a quartet centered at about 7.38 ppm, and the multiplet centered at 7.9 ppm is assigned to the phenyl and H₄ protons. The two H-C-N protons (H_b)

		Со			Ni			Zn		
[M(nca ₂ en)X ₂], X	Cl	Br	Ι	Cl	Br	Ι	Cl	Br	Ι	
IR spectra C=N (cm ⁻¹) NO ₂ (cm ⁻¹) UV-Vis spectra	1629	1633	1636	1635	1631	1639	1633	1632	1637	
·	645(2.78) 638(2.80) 585(3.10) 321(3.10)	650(3.00) 605(3.01) 577(3.20) 325(4.51)	689(2.32) 633(2.225) 590(3.10) 328(4.91)	510(2.22) 320(4.65)	513(2.30) 323(4.68)	547(2.69) 325(3.84)	323(4.243)	325(3.29)	329(4.73)	
CHN analysis %C, Calcd (found) %N, Calcd (found) %H, Calcd (found) ¹ H-NMR spectra H1 H2 H3 Ar-H, H4 ¹³ C-NMR spectra N ¹³ CH ₂ ¹³ CH ₂ N C=N Other carbons	 47.27(47.28) 11.02(11.00) 3.57(3.56) 	40.23(40.26) 9.38(9.37) 3.04(3.05)	34.76(34.75) 8.11(8.10) 2.63(2.63)	47.29(47.28) 11.03 3.57	40.24(40.25) 9.39(9.38) 3.04(3.04)	34.77(37.75) 8.11(8.12) 2.63(2.64)	46.67(46.69) 10.89(10.88) 3.53(3.54) 4.00(s, 4H) 8.37(d, 2H) 7.36(q, 2H) 7.55-8.10(m, 10H) 61.59 163.83 124.83, 127.13, 128.87, 129.07, 131.29, 132.60, 136.59, 147.90	39.80(30.81) 9.28(9.28) 3.01(3.02) 4.03(s, 4H) 8.37(d, 2H) 7.38(q, 2H) 7.58-8.9 (m, 10H) 62.30 164.25 124.90, 127.25, 128.88, 129.15, 131.32, 132.65, 136.63, 147.98	34.44(34.43) 8.03(8.04) 2.60(2.07) 4.04(s, 4H) 8.38(d, 2H) 7.41(q, 2H) 7.59-8.13(m, 10H) 62.26 164.14 124.89, 127.68, 128.63, 129.28, 131.21, 132.69, 136.82, 148.10	

 TABLE 1

 Selected bond lengths [Å] and bond angles [°] for 1b, 1c, and 2a

appear as a doublet at about 8.37 ppm. In the ¹H-NMR spectra of compounds **7–9**, the hydrogen of the imine CH groups (H_a) exhibits a downfield shift relative to the free ligand and shows no significant difference by changing the anion.

In the ¹H NMR spectra of compounds **7–9**, the hydrogen 3 groups (H18 in Fig. 2) exhibits a downfield shift relative to the free ligand and shows no significant difference by changing the anion. Nevertheless, the signals due to H₃ protons appear at 7.36, 7.38, and 7.41 ppm for ZnLCl₂, ZnLBr₂, and ZnLl₂ respectively (Table 1). In search for an explanation for this behavior, we have found no interaction between H₃ and the chloride atoms in ZnLCl₂.

However, the observed variation in the H_3 chemical shifts could be attributed to an intramolecular interaction with metal atom in the form of C-H···M weak hydrogen bonds (see more details in the crystal structures). Such interactions have also been reported by others.^[19,20] The extent of interaction depends on the steric restrictions imposed by the coordinated anion and the electron density of metal atom. The shielding effect resulting from this intramolecular interaction is strongest for Cl followed by Br and I coordinated to the metal atom.

The ¹³C-NMR spectrum of the free ligand exhibits 10 signals due to the phenyl rings and the ethylenic protons. In the ¹³C-NMR spectra of the complexes 6-9, the carbon atoms adjacent to the donor nitrogen atoms show downfield shift in their positions as compared with the free ligand, clearly indicating the coordination of the ligand and retention of the structure in the chloroform solutions.^[23]

UV-Vis Spectra

The UV-Vis spectral data of $M(nca_2en)X_2$ complexes are presented in Table 1. The Co $(nca_2en)Cl_2$ show three closely spaced weak bands in the visible region and a very intense band in the UV region. In the regular tetrahedral and near-tetrahedral Co(II) complexes only one d-d transition $[{}^{4}A_2(F) \rightarrow {}^{4}T_1(P)$, assigned as $\nu_3]$ is observed in the visible region. This transition has been reported for the tetrahedral $[Co(NCS)_4]^{2-}$ at 615 nm and for the pseudotetrahedral $[Co(morpholine)_2(NCS)_2]$ at 616 nm.^[11,21–23] The three



FIG. 2. ORTEP view of the crystal structure of $[Zn(nca_2en)Br_2]$, **8** showing the atom labeling scheme. The thermal ellipsoids enclose 50% of the electronic density.

 TABLE 2

 Crystal data and structure refinement for 8

Empirical formula: C20H18Br2N4O4Zn Formula weight = 603.57Crystal structure: monoclinic Space group: P21/n Z = 4a = 7.8386(12) Åb = 16.381(3) Åc = 18.226(3) Å $\alpha = 90^{\circ}$ $\beta = 100.054(12)^{\circ}$ $\gamma = 90^{\circ}$ $V = 2304.3(7) Å^3$ Calculated density = 1.740 Mg/m^3 Absorption coefficient/mm⁻¹ = 4.567 Temperature = 293(2) K F(000) = 1192Crystal size = $0.45 \times 0.25 \times 0.15 \text{ mm}^3$ No. of reflection used = 4394No. of parameters = 280 λ (Mo-K α) = 0.71073 Å $\theta_{\rm max} = 25.72^{\circ}$ $R1 = 0.0585[I \ge 2\sigma(I)]$ wR2 = 0.1273Goodness-of-fit on $F^2 = 1.067$ $(\Delta/\sigma)_{\rm max} = 0.001$ $(\Delta/\rho)_{\rm max} = 0.857 \text{ e}\text{\AA}^{-3}$ $(\Delta/\rho)_{\rm min} = -0.720 \ {\rm e}{\rm \AA}^{-3}$

closely spaced transitions in the spectrum of $Co(nca_2en)X_2$ complexes arise from the distortion in the tetrahedral symmetry around the metal center. This splitting originates from the reduction of the orbital degeneracy due to the difference in the ligand field strength of imine and halides donor atoms and the restricted bite angle of the N(1)-M-N(2) chelating ligand.^[11,21,23–25]

The intensity of the UV-band is consistent with its being a ligand-centered $\pi \rightarrow \pi^*$ transition or/and a charge-transfer transition. The ${}^{3}T_1(F) \rightarrow {}^{3}T_1(P)$ transition^[26,27] in

TABLE 3	
Selected bond length and bond angle of complex 8	

Zn(1)-N(3)	2.036(4)	C(6)-C(7)	1.517(9)
Zn(1)-N(2)	2.071(5)	C(7)-C(8)	1.440(8)
$\operatorname{Zn}(1)$ -Br (1)	2.3328(11)	C(8)-C(9)	1.333(8)
Zn(1)-Br(2)	2.3652(12)	C(10)-C(11)	1.469(8)
N(3)- $Zn(1)$ - $N(2)$	82.57(18)	N(3)-Zn(1)-Br(2)	112.20(15)
N(3)- $Zn(1)$ - $Br(1)$	116.69(14)	N(2)-Zn(1)-Br(2)	106.73(15)
N(2)-Zn(1)-Br(1)	115.96(15)	Br(1)-Zn(1)- Br(2)	117.37(4)

				2a			
1b		1c		Ι		II	
N1-C1-C2-N2	0.0(3)	N2-C1-C2-N1	- 12.2(9)	N1-C8-C9-C10	174.4(5)	N3-C57-C58-N4	4.2(9)
N1-C1-C2-C3	178.3(2)	N2-C1-C2-C3	169.2(6)	N1-C8-C9-C10	174.4(5)	N3-C57-C58-C59	-171.4(6)
Cu-N1-C1-C2	3.6(3)	Cu1-N1-C2-C1	3.9(7)	Cu1-N1-C8-C9	4.1(6)	Cu2-N3-C57-C58	0.1(7)
C1-C2-C3-C4	-177.0(2)	C1-C2-C3-C4	-179.0(6)	C1-C2-C3-C4	179.8(6)	C57-C58-C59-C60	175.9(7)
Cu-N2-C2-C1	-3.4(2)	Cu1-N2-C1-C2	13.3(7)	Cu1-N2-C9-C8	2.7(6)	Cu2-N4-C58-C59	169.7(6)
N1-Cu-N2-C2	4.01(14)	N2-Cu1-N1-C2	2.1(4)	N1-Cu1-N2-C9	-0.5(4)	Cu2-N3-C57-C58	0.1(7)

Ni(nca₂en)X₂ complexes (4, 5), appears as a low intensity band at 510 nm which is similar to that reported for Ni(Me4propylenediamine)₂Cl₂ (512 nm).^[21] A strong band at 320 nm is assigned to a ligand-centered $\pi \rightarrow \pi^*$ transition or/and a charge-transfer transition. The electronic spectral data conform to the structures determined by X-ray crystallography for cobalt and nickel complexes.^[12,13] The electronic absorption spectra of the Zn(nca₂en)X₂ complexes (7–9) in chloroform, are dominated by the broad band in the region 325 nm corresponding to the intra-ligand transition of nca₂en or/and a charge-transfer transition. No d-d transition are expected for d¹⁰ Zn(II) complexes.

Crystal Structure of Zn(nca₂en)Br₂, 8

The crystallographic and refinement data are summarized in Table 2 and the selected bond distances and angles are given in Table 3. The molecular structure of 8 is illustrated in Fig. 2, where metal atom is coordinated by the bidentate Schiff base ligand and two halogen atoms. While a tetrahedral geometry might be expected for a fourcoordinated Zn(II) center, the geometry about Zn(II) in 2 is distorted by the restricting bite of chelating ligand (Table 4). For **8** (see Fig. 2), the N(3)-Zn(1)-N(2) angle is only 82.57(18)° being in the range of 82-89° found for ethylenediamine chelated complexes.^[23,28] The Br(1)-Zn(1)-Br(2) angle is 117.37(4)° but the Br(1)-Zn(1)-N(3) angle, 116.69(14)°, is larger than the tetrahedral values. The average Zn-Br bond length of 2.35 Å agrees well with the same distance in other tetrahedral cobalt complexes. The Zn-N_{av} of 2.05 Å is being normal.^[26,28]

The ligand adopts a Z,Z configuration in these complexes. The mean value for dihedral angles N=C-C=C is about 175.5 indicating the planarity of this moiety for the complexes studied here. However, the N=C-C=C moieties in each complex are not coplanar, but showing parallel configuration. The single bond distance C(9)-C(8) in 8 (1.440(8) Å) being slightly shorter than C(10)-C(11) in 8 (1.517 Å) indicating an extended electron delocalization in these complexes. Due to the geometrical restrictions in 8 the H13 atom, lie in the vicinity of the metal atoms making intramolecular interactions possible in the form of weak C-H···M hydrogen bond. This type of interaction is somewhat similar to the agnostic interactions found in many organometallic complexes,^[29,30] although a C-H···M charge-assisted hydrogen bonding could be encountered here. As a matter of fact, the involvement of the metal centers in hydrogen bonding is now well established and known as nontraditional hydrogen bonds.^[31,32] A recent survey by Desiraju and Steiner,^[33] gives the range 2.5–3.2 Å for the weak C-H···M hydrogen bonds. Our structural data reveals that the C-H···M interactions is about 3 Å (C(8)-H(8)···Zn(1), 2.98 Å and C(13)-H(13)···Zn(1), 3.031 Å) in 8 would meet the above criteria and can be regarded as intramolecular weak hydrogen bonds.

Consequently, the vinilic protons are influenced by the change in the electron density on the central metal atom and this can be followed easily by ¹H NMR spectroscopy. Our results from ¹H NMR study of $Zn(nca_2en)X_2$ complexes, in which X = Cl, Br, I, clearly give further evidence to the existence of such C-H···M intramolecular interactions, although being weak but can be significant. This type of interaction has also been reported by others^[19,23,26,34,35] for closely related structures.

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