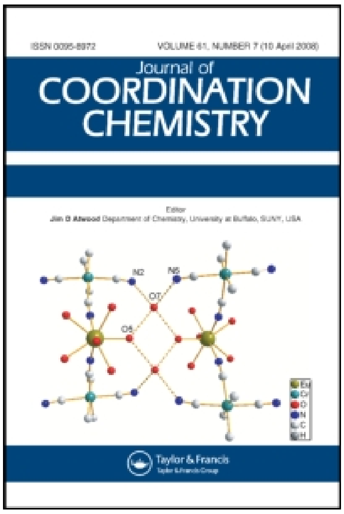

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Synthesis and Characterization of Cobalt(II), Nickel(II), and Zinc(II) Complexes with N,N '-bis(Trans- Cinnamaldehyde)-1,2-Diiminoethane Ligand, (ca 2 en): Crystal and Molecular Structures of Co(ca 2 en)Cl 2 , Co(ca 2 en)Br 2 and Ni(ca 2 en)Br 2

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SYNTHESIS AND CHARACTERIZATION OF COBALT(II), NICKEL(II), AND ZINC(II) COMPLEXES WITH *N,N′*-bis(*TRANS*-CINNAMALDEHYDE)-1,2-DIIMINOETHANE LIGAND, (ca_2en): CRYSTAL AND MOLECULAR STRUCTURES OF $Co(ca_2en)Cl_2$, $Co(ca_2en)Br_2$ AND $Ni(ca_2en)Br_2$

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A series of new complexes of the Schiff base obtained from *trans*-cinnamaldehyde and 1,2-diaminoethane (en) with the general formula of $M(ca_2en)X_2$ ($M = Co(II), Ni(II), Zn(II)$; $X = Cl, Br, I, NCS, N_3$; $(ca_2en) =$ *N,N′*-bis(*trans*-cinnamaldehyde)-1,2-diiminoethane) have been synthesized and characterized. The crystal structures of three *pseudo*-tetrahedral complexes, $Co(ca_2en)Cl_2$ (**1**), $Co(ca_2en)Br_2$ (**2**), and $Ni(ca_2en)Br_2$ (**5**), were determined by X-ray diffraction. Crystal data for **1**, $Co(ca_2en)Cl_2$: monoclinic; space group $P2_1/c$; $a = 7.1925(14)$ Å, $b = 20.327(4)$ Å, $c = 14.029(3)$ Å; $\beta = 95.06(3)^\circ$; $V = 2043.1(7)$ Å^3; $Z = 4$; and final $R_1 = 0.0381$ ($wR_2 = 0.0718$) for 4653 independent reflections with $I > 2\sigma(I)$ and 226 parameters; **2**, $Co(ca_2en)Br_2$; monoclinic, space group $P2_1/c$; $a = 7.3780(6)$ Å, $b = 20.4372(17)$ Å, $c = 14.1649(12)$ Å; $\beta = 94.902(2)^\circ$; $V = 2128.1(3)$ Å^3; $Z = 4$; and final $R_1 = 0.0491$ ($wR_2 = 0.1052$) for 5858 independent reflections with $I > 2\sigma(I)$ and 227 parameters; **5**, $Ni(ca_2en)Br_2$: monoclinic, space group $P2_1/c$; $a = 7.2388(6)$ Å, $b = 20.4651(16)$ Å, $c = 14.2782(12)$ Å; $\beta = 94.160(2)^\circ$; $V = 2109.6(3)$ Å^3; $Z = 4$; $R_1 = 0.0481$ ($wR_2 = 0.0907$) for 5914 independent reflections with $I > 2\sigma(I)$ and 227 parameters. The structures consist of discrete molecules in which the coordination polyhedra about the central metal ion are highly distorted tetrahedra with Cl(1)–Co–Cl(2), 115.51(3)°; N(1)–Co–N(2), 83.71(7)°; Br(1)–Co–Br(2), 114.58(4)°; N(1)–Co–N(2), 84.92(19)°; and Br(1)–Ni–Br(2), 125.23(3)°; N(1)–Ni–N(2), 85.11(15)° in **1**, **2**, and **5**, respectively. The stiryl groups are *cis*-endo with respect to the metal atom and the chelate ring is puckered. Utilization is made of electronic and vibrational spectra in structural diagnosis of other complexes.

Keywords: Cobalt(II); Nickel(II); Zinc(II); Schiff-base complex; *N,N′*-bis(*trans*-cinnamaldehyde)-1,2-diiminoethane; *Pseudo*-tetrahedral; Crystal structure

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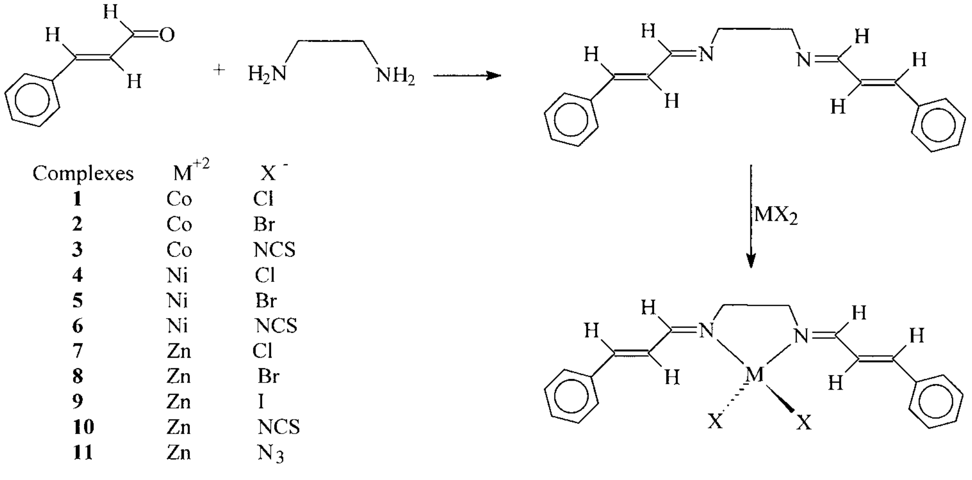

Complexes	M^{+2}	X^-
1	Co	Cl
2	Co	Br
3	Co	NCS
4	Ni	Cl
5	Ni	Br
6	Ni	NCS
7	Zn	Cl
8	Zn	Br
9	Zn	I
10	Zn	NCS
11	Zn	N_3

SCHEME 1

INTRODUCTION

The chemistry of the transition metal complexes of Schiff-base ligands has played an important role in the development of coordination chemistry as a whole [1]. In this context, a great deal of information regarding the properties of synthetic Schiff-base ligands of potential interest has been accumulated during the last decades. Several of these compounds have been characterized and used as models for biological systems [2]. Some series of complexes have also been applied to catalytic reactions [3]. Bidentate ligands containing imine groups have been investigated as modulators of the structural and electronic properties of transition metal centers [4].

As part of our continuing interest in the synthesis and properties of transition metal complexes with Schiff-base ligands [5], we have prepared and characterized several complexes of the type $M(ca_2en)X_2$ and determined the structures of $Co(ca_2en)Cl_2$ **1**, $Co(ca_2en)Br_2$ **2**, and $Ni(ca_2en)Br_2$ **5**. In this article we report the spectroscopic and structural properties of these complexes and discuss the effect of ligand constraint on distorting the environment of the metal ions, Co(II) and Ni(II), in MN_2X_2 complexes.

EXPERIMENTAL

Materials and Methods

All reagents and solvents were purchased from Aldrich and Merck and used as received unless otherwise noted. Ethylenediamine was distilled from potassium hydroxide under nitrogen and *trans*-cinnamaldehyde was distilled from anhydrous sodium sulfate before use. ^{1}H-NMR spectra were obtained on a BRUKER AVANCE DRX500 (500 MHz) spectrometer. Proton chemical shifts are reported in parts per million(ppm) relative to an internal standard of Me_4Si. UV–Vis spectra in solution were measured by a Shimadzu 240 spectrophotometer. IR spectra were recorded as KBr pellets on a Shimadzu 435. Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer.

Preparation of ligand *N,N'*-bis(*trans*-cinnamaldehyde)-1,2-diiminoethane (ca_2en)

For 100 years this readily prepared diimine was in the literature [6]; however, to use it as a bidentate ligand it was synthesized with some modifications and characterized by spectroscopic methods. To a stirring solution of *trans*-cinnamaldehyde (12.61 mL, 0.1 mol) in methanol (100 mL) cooled with an ice bath, was added dropwise 3.35 mL (0.05 mol) ethylenediamine. The mixture was then stirred for an additional 45 min, and finally poured into a beaker containing 500 mL of water. The new mixture was allowed to stir for 10 min, and the resulting white solid was collected on a coarse fritted glass funnel, washed with 3 portions of water, and dried in air for 48 h. The product was recrystallized from acetone and the resulting white crystals were collected and washed with cold acetone. Yield: 2.8 g (75%). mp: 108°C. Anal. Calcd. for $C_{20}H_{20}N_2$ (%): C, 83.29; H, 6.99; N, 9.86. Found: C, 83.10; H, 6.82; N, 9.73. ^{1}H-NMR (500 MHz, CD_3CN) 3.74 ($4H_a$, s, NCH_2CH_2N), 6.87 (2H, dd, $^3J_{HH} = 16$ Hz, $^3J_{HH} = 9$ Hz, 2CH=C*H*–CH), 7.04 (2H, d, $^3J_{HH} = 16$ Hz, 2PhC*H*=CH), 7.32–7.45, 7.45–7.56 (10H, *m*, 2Ar*H*), 8.05 ($2H_b$, d, $^3J_{HH} = 9$ Hz, 2CH–C*H*=N).

Preparation of $Co(ca_2en)Cl_2$ 1

To a solution of 0.70 g (2.4 mmol) ca_2en in 100 mL CH_2Cl_2 was added 0.31 g (2.4 mmol) of anhydrous $CoCl_2$, and the solution was stirred at room temperature for 3 h. The reaction mixture was filtered and the filtrate was left undisturbed in the hood for 24 h to give blue crystals. The product was collected by filtration and then recrystallized from dichloromethane. Needle-like, blue crystals were collected and washed with dichloromethane and dried *in vacuo*. Yield: 70%. Anal. Calcd. for $C_{20}H_{20}N_2Cl_2Co$ (%): C, 57.45; H, 4.80; N, 6.70. Found: C, 58.10; H, 4.70; N, 6.60.

Preparation of $Co(ca_2en)Br_2$ 2

This complex was prepared by a procedure similar to **1** except that 2.4 mmol of anhydrous $CoBr_2$ was used as the metal salt. Deep green crystals were collected by filtration and dried *in vacuo*. Yield: 63%. Anal. Calcd. for $C_{20}H_{20}N_2Br_2Co$ (%): C, 47.73; H, 3.98; N, 5.53. Found: C, 47.90; H, 3.91; N, 5.43.

Preparation of $Co(ca_2en)(NCS)_2$ 3

This complex was prepared by a procedure similar to **1** except that 2.4 mmol of $Co(NCS)_2$ was used as the metal salt and the product was recrystallized from dichloromethane-*n*-butanol (5 : 1 v/v). Green crystals were collected and dried *in vacuo*. Yield: 78%. Anal. Calcd. for $C_{22}H_{20}N_4S_2Co$ (%): C, 57.02; H, 4.32; N, 12.09. Found: C, 56.60; H, 4.50; N, 12.30.

Preparation of $Ni(ca_2en)Cl_2$ 4

To a solution of 0.288 g (1 mmol) ca_2en in 10 mL diethylether was added a solution of 0.218 g (1 mmol) of anhydrous $NiCl_2$ in 30 mL acetonitrile, and the solution was stirred at room temperature for 2.5 h. The product precipitated as a pink powder and was collected by filtration. The crude product was recrystallized from dichloromethane by diffusion of ether vapor into the solution. Yield: 58%. Anal. Calcd. for $C_{20}H_{20}N_2Cl_2Ni$ (%): C, 57.46; H, 4.79; N, 6.79. Found: C, 57.30; H, 4.70; N, 6.59.

Preparation of Ni(ca$_2$en)Br$_2$ 5

To a stirring solution of 0.53 g (2.4 mmol) of anhydrous $NiBr_2$ in 80 mL acetonitrile was added dropwise a solution of 0.70 g (2.4 mmol) ca$_2$en in 50 mL chloroform, and the solution was stirred for an additional 30 min at room temperature. The solvent was evaporated on a rotary evaporator at 40°C. The solid residue was dissolved in 50 mL chloroform and filtered. The filtrate was left overnight to give pink-red crystals. The product was collected by filtration and recrystallized from chloroform. Yield: 76%. Anal. Calcd. for $C_{20}H_{20}N_2Br_2Ni$ (%): C, 47.40; H, 3.98; N, 5.53. Found: C, 48.30; H, 3.78; N, 5.42.

Preparation of Ni(ca$_2$en)$_2$(NCS)$_2$ 6

This complex was prepared by a procedure similar to **4** except that 3 mmol of anhydrous $Ni(NCS)_2$ was used as the metal salt. Brownish-green crystals were collected by filtration and dried *in vacuo*. Yield: 61%. Anal. Calcd. for $C_{22}H_{20}N_4S_2Ni$ (%): C, 57.04; H, 4.32; N, 12.10. Found: C, 56.95; H, 4.25; N, 12.00.

Preparation of Zn(ca$_2$en)Cl$_2$ 7

To a solution of 0.270 g (2 mmol) $ZnCl_2$ in 30 mL methanol was added a solution of 0.721 g (2.5 mmol) ca$_2$en in 30 mL methanol and stirred at room temperature for 3 h. The product precipitated as a white powder and was collected by filtration. The crude product was recrystallized from acetone to give white needle-like crystals. Yield: 79%. Anal. Calcd. for $C_{20}H_{20}N_2Cl_2Zn$ (%): C, 56.55; H, 4.71; N, 6.60. Found: C, 56.40; H, 4.80; N, 6.60.

Preparation of Zn(ca$_2$en)Br$_2$ 8

This complex was prepared by a procedure similar to that for Zn(ca$_2$en)Cl$_2$ except that 0.445 g of $ZnBr_2$ was used as the metal salt. Yield: 67%. Anal. Calcd. for $C_{20}H_{20}N_2Br_2Zn$ (%): C, 46.78; H, 3.92; N, 5.44. Found: C, 48.10; H, 3.84; N, 5.35.

Preparation of Zn(ca$_2$en)I$_2$ 9

This complex was prepared by a procedure similar to that for Zn(ca$_2$en)Cl$_2$ except that 0.640 g of ZnI_2 was used as the metal salt. Yield: 72%. Anal. Calcd. for $C_{20}H_{20}N_2I_2Zn$ (%): C, 39.45; H, 3.32; N, 4.61. Found: C, 39.70; H, 3.30; N, 5.42.

Preparation of Zn(ca$_2$en)(NCS)$_2$ 10 and Zn(ca$_2$en)(N$_3$)$_2$ 11

To a solution of 0.262 g (1 mmol) $Zn(NO_3)_2$ in 25 mL ethanol was added a solution of 0.194 g (2 mmol) of KSCN or 0.130 g (2 mmol) of NaN_3 in 10 mL ethanol and the solution was stirred for 20 min. The resulting white KNO_3 or $NaNO_3$ salt was filtered off and a solution of 0.290 g (1 mmol) of ca$_2$en in 5 mL methanol was added to the filtrate and the mixture stirred for 30 min. The product was precipitated as a white powder and collected by filtration and dried in air. Yield: 85 and 80%, respectively. Anal. Calcd. for $C_{22}H_{20}N_4S_2Zn$ (%): C, 56.23; H, 4.26; N, 11.93. Found: C, 56.60; H, 4.30; N, 11.70. Anal. Calcd. for $C_{20}H_{20}N_8Zn$ (%): C, 54.87; H, 4.57; N, 25.61. Found: C, 54.40; H, 4.50; N, 24.80%.

Crystallography

Suitable single crystals of [Co(ca$_2$en)Cl$_2$] **1**, [Co(ca$_2$en)Br$_2$] **2**, and [Ni(ca$_2$en)Br$_2$] **5**, were obtained by slow evaporation of a dichloromethane solution of **1** and **2** and a chloroform solution of **5** at room temperature.

An aquamarine-colored crystal of **1**, the habitus of which consisted of {100}, $\{01\bar{1}\}$ and {021} pinacoids, was measured at $T = 293$ K, on a Stoe IPDS system equipped with Mo radiation. A crystal-image-plate distance of 60 mm was chosen and two hundred images, in ϕ increments of 1°, were exposed for 5 min each. An inspection of reciprocal space ascertained that the diffraction figure consisted essentially of the spots corresponding to the cell given in Table I. For the integration, a mosaic spread of 0.008 and spot sizes between 17 and 21 pixels were used. The intensities were corrected for Lorentz and polarization effects and an absorption correction based on the habitus was carried out as well. The decay during the measurement was negligible. The structure was solved with the help of DIRDIF 96 [7], and refined by means of SHELXTL 5.05 [8]. All nonhydrogen atoms were refined anisotropically, and all hydrogens were made to ride on their associated carbons.

A piece of a long turquoise crystal of **2** was cut and brought onto a Bruker SMART CCD system equipped with graphite-monochromatized Mo radiation. Its habitus consisted of a {011} prism and a {100} pinacoid. A hemisphere of reflections was collected as ω scans; a crystal-CCD distance of 45 mm was chosen and the frames were exposed for 60 s each. Using the SAINT [9] package, the lattice constants were optimized (Table I) and intensities were integrated and corrected for Lorentz and polarization effects. A numerical absorption correction based on the habitus was computed with the help of the XPREP [8] program. The decay during the measurement was negligible. The structure was solved with the help of DIRDIF 96 [7], and refined by means of SHELXTL 5.05 [8]. All nonhydrogen atoms were refined anisotropically, and all hydrogens were made to ride on their associated carbons.

A piece of a long lilac crystal of **5** was cut and brought onto a Bruker SMART CCD system equipped with graphite-monochromatized Mo radiation. Its habitus consisted of a {011} prism and (751) and $(\overline{751})$ facture planes. A hemisphere of reflections was collected as ω scans; a crystal-CCD distance of 45 mm was chosen and the frames were exposed for 60 s each. Using the SAINT [9] package, the lattice constants were optimized (Table I) and intensities were integrated and corrected for Lorentz and polarization effects. A numerical absorption correction based on the habitus was computed with the help of the XPREP [8] program. The decay during measurement was negligible. The structure was solved with the help of DIRDIF 96 [7], and refined by means of SHELXTL 5.05 [8]. All nonhydrogen atoms were refined anisotropically, and all hydrogens were made to ride on their associated carbons.

TABLE I Crystallographic and refinement data for Complexes **1**, **2** and **5**

Empirical formula	$C_{20}H_{20}Cl_2CoN_2$	$C_{20}H_{20}Br_2CoN_2$	$C_{20}H_{20}Br_2N_2Ni$
Formula weight	418.21	507.13	506.91
Temperature (K)	293(2)	293(2)	293(2)
Crystal size (mm)	0.6 × 0.17 × 0.13	0.66 × 0.14 × 0.10	0.48 × 0.22 × 0.14
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system and space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a [Å]	7.1925 (14)	7.3780(6)	7.2388(6)
b [Å]	20.327(4)	20.4372(17)	20.4651(16)
c [Å]	14.029(3)	14.1649(12)	14.2782(12)
α [°]	90	90	90
β [°]	95.06(3)	94.902(2)	94.160(2)
γ [°]	90	90	90
V [Å^3]	2043.1(7)	2128.1(3)	2109.6(3)
Z	4	4	4
D (calc.) [g cm^{-1}]	1.360	1.583	1.596
μ [mm^{-1}]	1.106	4.566	4.712
F (000)	860	1004	1008
Θ range (°)	2.48–28.03	1.75–30.00	1.74–30.00
Index ranges	$-8 \leq h \leq 8$, $-26 \leq k \leq 26$, $-18 \leq l \leq 18$	$-9 \leq h \leq 10$, $-24 \leq k \leq 27$, $-19 \leq l \leq 17$	$-9 \leq h \leq 10$, $-28 \leq k \leq 21$,$-18 \leq l \leq 17$
Refls collected.	19415	14904	15011
Independent reflection	4653 [$R_{int} = 0.0572$]	5858 [$R_{int} = 0.0452$]	5914 [$R_{int} = 0.0595$]
Completeness to Θ	n/a	30.00, 94.5%	30.00, 96.1%
Absorption correction	Integration	Integration	Integration
Maximum and minimum transmission	0.9012, 0.7799	0.6542, 0.2481	0.5615, 0.1800
Refinement method	Full-matrix least squares on F^2	Full-matrix Least squares on F^2	Full-matrix Least-squares on F^2
Data/restraints/parameters	44651/0/226	5858/0/227	5914/0/227
Goodness-of-fit on F^2	1.923	2.251	1.784
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0381$, $wR_1 = 0.0718$	$R_1 = 0.0491$ $wR_2 = 0.1052$	$R_1 = 0.0481$ $wR_2 = 0.0907$
R indices (all data)	$R_1 = 0.0576$, $wR_2 = 0.1028$	$R_1 = 0.1203$, $wR_2 = 0.1068$	$R_1 = 0.1219$, $wR_2 = 0.0931$
Extinction coefficient	n/a	0.0053(3)	0.00118(14)
Largest different Peak and hole [e Å^{-3}]	0.381 and −0.302	1.143 and −0.422	0.845 and −0.414

[*]$R_1 = \sum \|F_o| - |F_C\| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Crystal data and other experimental details are summarized in Table I. Coordinates for selected atoms are given in Tables II, III, and IV for **1**, **2**, and **5** respectively. Selected bond distances and angles are given in Table V.

RESULT AND DISCUSSION

X-Ray Structure

The molecular structures of Co(ca$_2$en)Cl$_2$ **1**, Co(ca$_2$en)Br$_2$ **2**, and Ni(ca$_2$en)Br$_2$ **5** with the atom-numbering schemes are presented in Figs. 1, 2, and 3, and selected interatomic parameters are collected in Table V. Co(ca$_2$en)Cl$_2$ **1**, and Co(ca$_2$en)Br$_2$ **2** consist of discrete monomeric molecules. The shortest intermolecular Co–Cl and Co–Br distances are 5.887 and 6.068 Å in **1** and **2**, respectively. The nearest Co–Co intermolecular

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Co(ca$_2$en)Cl$_2$ (**1**)[a]

Atom	*X*	*Y*	*Z*	U_{eq}
Co	950(1)	759(1)	3323(1)	52(1)
Cl(1)	3020(1)	586(1)	4562(1)	81(1)
Cl(2)	2130(1)	946(1)	1941(1)	96(1)
N(1)	−1193(2)	110(1)	3228(1)	50(1)
N(2)	−1057(2)	1414(1)	3630(1)	53(1)
C(1)	−1231(3)	−515(1)	3333(1)	52(1)
C(2)	419(3)	−917(1)	3505(1)	53(1)
C(3)	298(3)	−1565(1)	3613(1)	55(1)
C(4)	−971(3)	2036(1)	3767(1)	54(1)
C(5)	693(3)	2411(1)	3672(2)	57(1)
C(6)	813(3)	3057(1)	3857(2)	59(1)
C(7)	−2961(3)	478(1)	3109(2)	57(1)
C(8)	−2804(3)	1061(1)	3769(2)	60(1)
C(21)	2399(4)	3484(1)	3761(1)	61(1)
C(22)	2328(4)	4131(1)	4099(2)	79(1)
C(23)	3854(7)	4547(2)	4024(2)	104(1)
C(24)	5373(6)	4342(2)	3618(2)	103(1)
C(25)	5468(4)	3711(2)	3274(2)	90(1)
C(26)	3981(4)	3286(1)	3343(2)	69(1)
C(31)	1770(3)	−2038(1)	3816(1)	58(1)
C(32)	3613(4)	−1861(1)	4051(2)	69(1)
C(33)	4979(5)	−2342(2)	4243(2)	100(1)
C(34)	4485(7)	−3006(2)	4200(2)	113(1)
C(35)	2657(7)	−3184(2)	3988(2)	104(1)
C(36)	1318(4)	−2711(1)	3800(2)	73(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

approach is 5.092 Å in **1** and 5.178 Å in **2**. Deviations from idealized tetrahedral symmetry in Complex **1** are significant, especially for the N(1)–Co–N(2) angle which is only 83.71(7)°. This angle is in the range of 82–89° found for ethylenediamine chelate compounds [10,11]. The Cl(1)–Co–Cl(2) angle has opened up to 115.51(3)°. The N(1)–Co–Cl(1) (113.86(5)°) angle is also larger than the tetrahedral values. The Co–Cl average bond length of 2.216 Å agrees well with the analogous distance in other tetrahedral cobalt complexes: Co(ethylenedimorpholine)Cl$_2$, 2.23 Å and Co(*p*-toluidine)$_2$Cl$_2$, 2.26Å [11]. The average Co–N distance of 2.03 Å agrees with the 2.116 Å average for tetrahedral Co(ethylenedimorpholine)Cl$_2$ [11], and 2.038 Å for tetrahedral Co(*N*,*N*-bis(3,5-dimethylpyrazol-1-yl-methyl)aminobenzene)Cl$_2$ [12].

The geometry about the metal atom in Co(ca$_2$en)Br$_2$ is also approximately tetrahedral, with distortions indicated by the unequal metal–ligand bond lengths and angles (Table V), which is especially significant for N(1)–Co–N(2) angle, 84.92(19)°, and the deviation from 90° of the dihedral angle (91.4°) between the CoBr$_2$ and the CoN$_1$N$_2$ planes. The average Co–Br bond length of 2.354 Å and Co–N distance of 2.034 Å agree well with the analogous distances in other tetrahedral cobalt complexes, Co–Br = 2.347(2) Å and Co–N = 2.070(6) for tetrahedral Co(NITmepy)Br$_2$ [13].

The Co(II) complexes with bidentate Schiff-bases showing a distorted tetrahedral structure, are common both in the solid state and dissolved in noncoordinating solvents [14–16], and the observed *pseudo*-tetrahedral structures for Co(ca$_2$en)Cl$_2$ **1** and Co(ca$_2$en)Br$_2$ **2** are in accord with expectation. Considering a low structural preference energy for other geometries of d^7 and d^{10} ions, a distorted tetrahedral structure can be inferred for other Co(ca$_2$en)X$_2$, and all Zn(ca$_2$en)X$_2$ complexes.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Co(ca_2en)Br_2$ (**2**)[a]

Atom	*X*	*Y*	*Z*	U_{eq}
Co	867(1)	748(1)	3244(1)	56(1)
Br(1)	3011(1)	571(1)	4543(1)	83(1)
Br(2)	2135(1)	930(1)	1794(1)	96(1)
N(1)	−1222(6)	105(2)	3143(3)	53(1)
N(2)	−1060(6)	1419(2)	3545(3)	55(1)
C(1)	−1255(8)	−519(3)	3269(4)	58(2)
C(2)	322(8)	−922(3)	3462(4)	55(2)
C(3)	229(8)	−1558(3)	3618(4)	56(2)
C(4)	−932(8)	2039(3)	3698(4)	60(2)
C(5)	700(8)	2400(3)	3612(4)	58(2)
C(6)	80049(8)	3026(3)	3793(4)	63(2)
C(7)	−2939(7)	486(3)	2989(4)	63(2)
C(8)	−2784(7)	1071(3)	3659(4)	65(2)
C(21)	2422(10)	3441(3)	3726(4)	63(2)
C(22)	2408(11)	4068(4)	4082(4)	84(2)
C(23)	3929(17)	4474(4)	4044(6)	116(4)
C(24)	5386(15)	4255(5)	3631(6)	115(4)
C(25)	5451(10)	3643(4)	3252(5)	91(2)
C(26)	3944(10)	3231(3)	3307(4)	76(2)
C(31)	1698(9)	−2026(3)	3858(4)	56(2)
C(32)	3486(10)	−1834(3)	4087(4)	72(2)
C(33)	4824(10)	−2307(5)	4308(5)	93(2)
C(34)	4380(15)	−2954(5)	4277(6)	111(3)
C(35)	2636(15)	−3130(4)	4070(5)	104(3)
C(36)	1297(10)	−2687(3)	3858(4)	75(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ni(ca_2en)Br_2$ (**5**)[a]

Atom	*X*	*Y*	*Z*	U_{eq}
Ni	860(1)	729(1)	3230(1)	59(1)
Br(1)	28(1)	564(1)	4568(1)	81(1)
Br(2)	1781(1)	886(1)	1710(1)	107(1)
N(1)	−1200(5)	99(2)	3143(3)	54(1)
N(2)	−1058(5)	1378(2)	3555(3)	56(1)
C(1)	−1193(6)	−531(2)	3248(3)	61(1)
C(2)	456(6)	−936(2)	3447(3)	59(1)
C(3)	366(7)	−1572(2)	3584(3)	57(1)
C(4)	−928(7)	1992(2)	3707(3)	59(1)
C(5)	717(7)	2356(2)	3610(3)	59(1)
C(6)	818(7)	2981(2)	3799(3)	60(1)
C(7)	−2959(6)	456(2)	3015(4)	64(1)
C(8)	−2795(6)	1046(2)	3679(4)	71(2)
C(21)	2373(8)	3406(2)	3728(3)	60(1)
C(22)	2362(8)	4035(3)	4074(4)	80(2)
C(23)	3949(13)	4448(3)	4013(5)	107(3)
C(24)	5445(10)	4183(5)	3589(6)	124(3)
C(25)	5440(12)	3580(4)	3246(5)	112(3)
C(26)	3939(9)	3206(3)	3322(4)	79(2)
C(31)	1886(8)	−2009(2)	3830(3)	57(1)
C(32)	3680(8)	−1801(3)	4094(4)	70(1)
C(33)	5067(9)	−2236(4)	4307(4)	96(2)
C(34)	4689(12)	−2881(4)	4272(5)	114(3)
C(35)	2918(12)	−3095(3)	4040(5)	108(2)
C(36)	1529(8)	−2668(3)	3812(4)	78(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE V Selected bond distances (Å) and angles (°) for Compounds (**1**), (**2**), and (**5**)

	(**1**)	(**2**)	(**5**)
M	*Co*	*Co*	*Ni*
X	*Cl*	*Br*	*Br*
M–N(1)	2.023(2)	2.021(4)	1.969(4)
M–N(2)	2.038(2)	2.047(5)	1.999(4)
M–X(1)	2.2151(10)	2.3490(10)	2.3356(9)
M–X(2)	2.2166(8)	2.3584(10)	2.3392(9)
N(1)–C(1)	1.280(3)	1.288(6)	1.297(5)
N(1)–C(7)	1.468(3)	1.487(6)	1.469(5)
N(2)–C(4)	1.280(3)	1.287(6)	1.277(5)
N(2)–C(8)	1.475(3)	1.479(6)	1.451(5)
C(1)–C(2)	1.444(3)	1.433(7)	1.464(6)
C(2)–C(3)	1.330(3)	1.322(7)	1.318(5)
C(3)–C(31)	1.439(3)	1.464(7)	1.442(6)
C(4)–C(5)	1.435(3)	1.426(7)	1.421(6)
C(5)–C(6)	1.338(3)	1.308(7)	1.308(5)
C(6)–C(21)	1.450(3)	1.447(8)	1.431(6)
C(7)–C(8)	1.508(3)	1.524(7)	1.534(6)
N(1)–M–N(2)	83.71(7)	84.92(19)	85.11(15)
N(1)–M–X(1)	113.86(5)	114.43(13)	112.23(11)
N(2)–M–X(1)	112.15(5)	111.93(13)	107.84(11)
N(1)–M–X(2)	113.72(6)	113.39(12)	107.25(11)
N(2)–M–X(2)	113.92(5)	114.23(13)	111.96(11)
X(1)–M–X(2)	115.51(3)	114.58(4)	125.23(3)
C(1)–N(1)–C(7)	119.1(2)	120.9(5)	120.4(4)
C(1)–N(1)–M	131.55(14)	131.1(4)	130.3(3)
C(7)–N(1)–M	109.02(13)	107.7(3)	109.1(3)
C(4)–N(2)–C(8)	119.4(2)	120.5(5)	119.5(4)
C(4)–N(2)–M	130.7(2)	130.7(4)	130.5(3)
C(8)–N(2)–M	109.73(13)	108.6(3)	109.9(3)

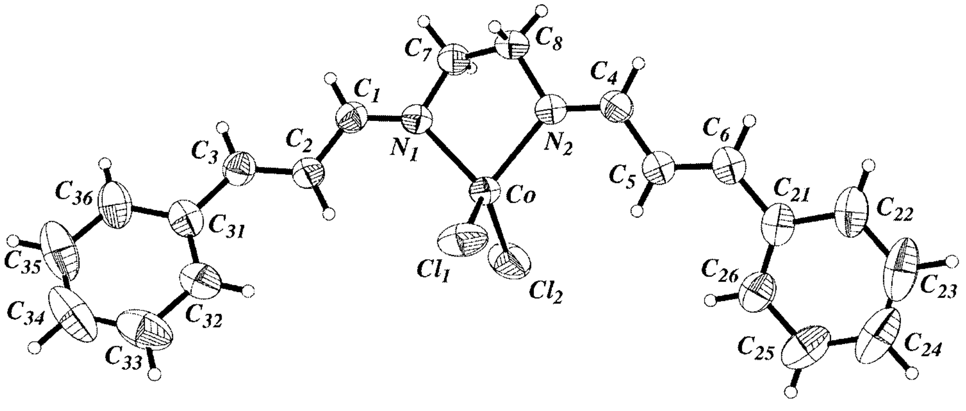

FIGURE 1 ORTEP diagram of $Co(ca_2en)Cl_2$ **1**.

Most nickel complexes with chelating ligands including Schiff-bases prefer tetragonal geometries [17–19]. However, the steric effects from ca_2en distort the geometry at nickel(II) in $Ni(ca_2en)Br_2$, **5**, to *pseudo*-tetrahedral (Fig. 3). $Ni(ca_2en)Br_2$ exists as discrete molecules of four-coordinate Ni(II) containing the bidentate Schiff-base ligand and two coordinated bromine atoms. The shortest intermolecular Ni–Br distance is 5.037 Å and the nearest Ni–Ni intermolecular approach is 6.075 Å. The structures for

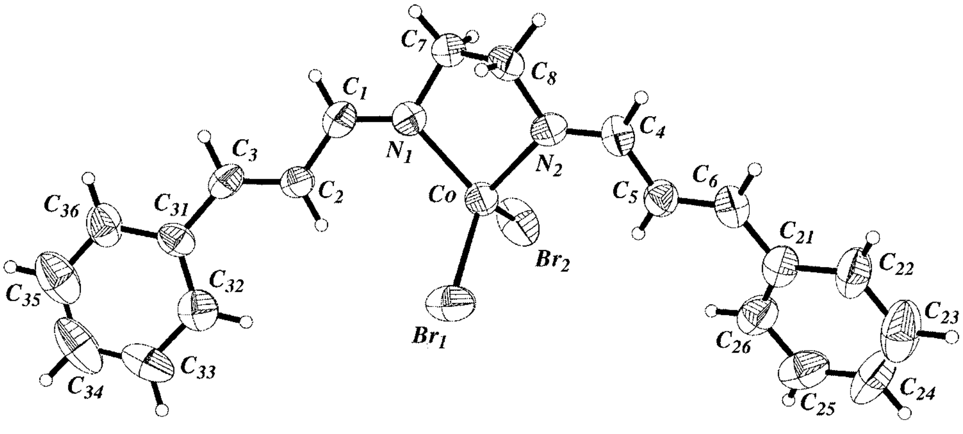

FIGURE 2 ORTEP diagram of Co(ca_2en)Br_2 **2**.

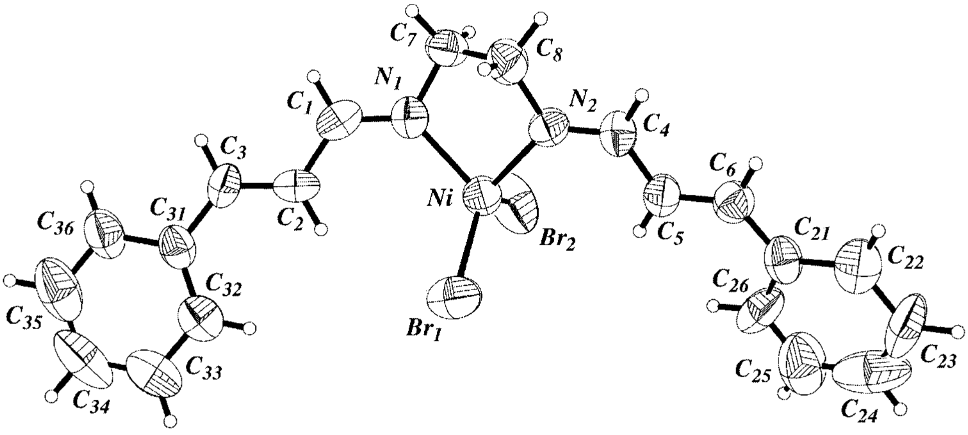

FIGURE 3 ORTEP diagram of Ni(ca_2en)Br_2 **5**.

various nickel complexes with bidentate ligands show a trend from dimeric for the chloro (i.e. the intermolecular Ni–Ni separation = 3.565 Å in [Ni(biq)Cl_2]$_2$ [20], and 3.581 in [{Ni(Cl)(Immepy)}$_2$(μ-Cl)$_2$]) [13] to monomeric for the bromo and iodo complexes (i.e. the nearest intermolecular Ni–Ni approach = 7.09 Å in [Ni($C_{20}H_{24}N_2$)Br_2] [21]). This is in keeping with the magnetic properties observed for these complexes. In each case the known dimeric complexes exhibit antiferromagnetic interactions. However, when large steric interactions are operative (such as in **1**, **2**, and **5**), the complexes are monomeric with magnetic moments corresponding to the unpaired electrons of the central metal ion in a tetrahedral environment.

Deviations from tetrahedral geometry are rather large, especially for the N(l)–Ni–N(2) and Br(1)–Ni–Br(2) angles which are 85.11(15) and 125.23(3)°, respectively. Except for the N(1)–Ni–N(2) and Br(1)–Ni–Br(2) angles, the bond angles formed at the nickel atom are all within 3° of the idealized tetrahedral angle (see Table V). The Ni–Br average bond length of 2.337 Å agrees with those reported for other tetrahedral nickel complexes: $Ni(PPh_3)_2Br_2$, 2.34 Å [22]; $Ni(biq)_2Br_2$, 2.34 Å [20]; $[(n\text{-}C_4H_9)_4N][Ni(C_9H_7N)Br_3]$, 2.38 Å [23]. The average Ni–N distances of 1.984 Å are similar to those in *pseudo*-tetrahedral bis(*N*-isopropylsalicylaldiminato)nickel(II), 1.97 Å [24], and Ni(II) imine complexes, ($Ni(biq)_2Br_2$, 1.99 Å [20], [Ni(TC-6,6)], 1.95 Å) [25], but are *ca.* 0.07 Å longer than those in tetragonal Ni(II) analogs [26,27]. In the tetragonal case, the $d_{x^2-y^2}$ orbital is vacant, allowing a closer approach of the ligands to the metal along the x and y axes.

Despite the fact that the donor nitrogen atoms are sp^2 hybridized, the chelate ring is significantly puckered in these complexes and some strain in the chelate ring is suggested by the deviation from the 120° angle about the nitrogen, Co–N(l)–C(7) (109.02(13)°) and Co–N(2)–C(8) (109.73(13)°); in **1**, Co–N(1)–C(7) (107.7(3)°) and Co–N(2)–C(8) (108.6(3)°) in **2**; and Ni–N(1)–C(7) (109.1(3)°) and Ni–N(2)–C(8) (109.9(3)°) in **5**. Linking carbon atom C(7) is 0.435 Å above the MN_2 plane defined by N(1)–M–N(2) in **1**, 0.488Å in **2** and 0.477Å in **5** while C(8) is 0.218 Å in **1**, 0.184 Å in **2**, and 0.180 Å in **5** below. The dihedral angle between the plane defined by N(1)–M–N(2) and X(1)–M–X(2) is 90.8° in **1**, 91.4° in **2**, and 93.6° in **5**, and is fairly typical for diamine chelates, 88.1° $Ni(C_{20}H_{24}N_2)Br_2$ [21], and 84.9° for $Ni(biq)Br_2$ [20].

The phenyl plane (C(21)→C(26)) and the chain connecting the ring to the coordinated nitrogen are roughly coplanar. The angle between the plane of the phenyl ring and the plane subtended by C(6)=C(5)–C(4)=N(2) is 10.4° in **1**, 11.7° in **2**, and 10.2° in **5**. This degree of coplanarity, which allows for increased π-conjugation in the ligand, is consistent with the observed C–C single bond distances in the coordinated ligand; C(4)–C(5), 1.435(3) Å < C(6)–C(21), 1.450(3) Å < C(7)–C(8), 1.508(3) Å for **1**; C(4)–C(5), 1.426(7) Å < C(6)–C(21), 1.447(8) Å < C(7)–C(8), 1.524(7) Å for **2**, and C(4)–C(5), 1.421(6) Å < C(6)–C(21), 1.431(6) Å < C(7)–C(8), 1.534(6) Å for **5**. In principle three conformations are possible for the coordinated ligand as presented in Scheme 1. The X-ray structure analysis indicates that the preferred conformation of the ligand in these complexes is *trans–trans*. This is in accord with the results obtained from the PMR and X-ray structure analysis of similar NiN_2X_2 complexes [21,28].

Spectral Studies

^{1}H-NMR data suggest that the ligand has a symmetrical structure with two imine groups. Four methylene protons are found at 3.85 ppm as a singlet. The four vinyl CH protons are observed as a multiplet centered at 6.95 ppm and the multiplet centered at 7.40 ppm is assigned to the ten phenyl protons. The two H–C=N protons appear as a doublet at 8.08 ppm. The important features of the IR and UV–Vis spectra for the ligand and its complexes are summarized in Table VI. The ν(C=N) band which appears at 1634 cm^{-1} in the free ligand shifts to lower frequency upon complexation. The frequencies at 2060, 2085, and 2072 cm^{-1} for compound **3**, **6**, and **10** indicate that NCS ligand in these complexes is probably N-bonded [29].

The electronic spectra of $Co(ca_2en)X_2$ in dichloromethane show three weak absorption bands in the visible region in addition to a very intense band in the UV region (Table VI). 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 intensity of the three closely spaced transitions in the visible region is characteristic of *d–d* transitions. Regular tetrahedral and near-tetrahedral Co(II) complexes have only one *d–d* transition

TABLE VI IR and UV-Vis. spectral data of M(ca$_2$en)X$_2$ complexes

	IR/cm^{-1}				*UV Vis*
Compound	*C=N*	*NCS*	*N$_3$*	*Solvent*	λ_{max}/nm (log ε/M^{-1}cm^{-1})
ca$_2$en	1634			Dichloromethane	284(4.90), 228(4.61)
Co(ca$_2$en)Cl$_2$ **1**	1630			Dichloromethane	657(2.73), 638(2.73), 579(3.00), 323(4.85)
Co(ca$_2$en)Br$_2$ **2**	1630			Dichloromethane	652(2.93), 601(2.93), 578(2.66), 324(4.75)
Co(ca$_2$en) (NCS)$_2$ **3**	1614	2060		Dichloromethane	623(2.59), 580(2.58), 330(4.82)
Ni(ca$_2$en)Cl$_2$ **4**	1626			Dichloromethane	520(2.26), 310(4.77)
Ni(ca$_2$en) Br$_2$ **5**	1628			Dichloromethane	515(2.28), 312(4.88)
Ni(ca$_2$en) (NCS)$_2$ **6**	1625	2085		Dichloromethane	520(2.02), 303(4.99)
Zn(ca$_2$en)Cl$_2$ **7**	1630			Acetone	314(4.92)
Zn(ca$_2$en) Br$_2$ **8**	1629			Acetone	313(4.93)
Zn(ca$_2$en)I$_2$ **9**	1628			Acetone	316(4.92)
Zn(ca$_2$en) (NCS)$_2$**10**	1632	2072		Acetone	335(4.87)
Zn(ca$_2$en) (N$_3$)$_2$ **11**	1627		2087	Acetone	340(4.85)

[$^4A_2(F) \rightarrow {}^4T_1(P)$] assigned as ν_3 in the visible region [30]. This transition is observed at 615 nm for the tetrahedral [Co(NCS)$_4$]$^{2-}$ and at 616 nm for the *pseudo*-tetrahedral [Co(morpholine)$_2$(NCS)$_2$] complexes [30]. The three closely spaced transitions in the spectra of Co(ca$_2$en)X$_2$ complexes arise from distortion in the tetrahedral symmetry around the metal center. This splitting originates from reduction of the orbital degeneracy due to the difference in the ligand field strength of imine and halide donor atoms and the restricted bond angle of the N(l)–M–N(2) chelating ligand [30,31].

Tetrahedral (T$_d$) nickel(II) complex spectra behave like the corresponding cobalt(II) and the *d–d* transition in the visible region is assigned to a $^3T_1(F) \rightarrow {}^3T_1(P)$ [22]. For Ni(ca$_2$en)X$_2$ this band appears at about 515 nm (Table V) which is similar to that reported for Ni(Me$_4$propylenediamine)$_2$Cl$_2$ (512 nm) [30]. No *d–d* transitions are expected for d^{10} Zn(II) complexes, however an intense intraligand transition is observed for all Zn(II) complexes in the UV region.

CONCLUSIONS

This study shows that the two imine nitrogens of ca$_2$en react with transition metal ions to produce stable complexes. The structure of this ligand has a directional effect on the geometry of the resulting complexes, leading to a *pseudo*-tetrahedral structure. This is interesting especially for Ni(II), which usually shows preferences for a tetragonal geometry.

Acknowledgments

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Supplementary Material

Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 182111 for **1**, 182112 for **2**, and 182113 for **5**.

Copies of this information may be obtained free of charge from The Director, 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).

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