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Diazoketiminato complexes of Au(III): syntheses, characterisation and structure

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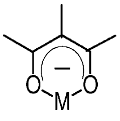
Abstract

A series of 2-(arylazo)aniline ligands were synthesised. The reaction of these ligands with $HAuCl_4$ afforded diazoketiminato complexes of Au(III). The ligands and complexes were characterised by ^1H NMR, IR and UV–Vis spectroscopic data. The X-ray structure of one of the complexes has been determined and the formation of a diazoketiminato species has been established.

Keywords: 2-(Arylazo)anilines; Gold(III) complex; Diazoketiminato species

1. Introduction

The transition metal chelates of ligands with delocalised π conjugation within the chelate ring have drawn much attention in recent years [1]. Among these ligand systems β-diketonates (**1**), β-enaminoketonates (**2**) and β-diketiminates (**3**) are noteworthy [2].



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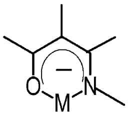

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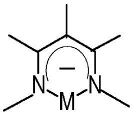

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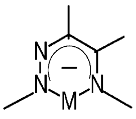

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Such anionic bidentate ligands bind the transition metals forming a six membered chelate ring with 6π electrons ($4n+2$ rule). Recently we have reported the palladium(II) chelate incorporating the diazoketiminato ligand (**4**) [3]. The ligand systems **1**, **2**, **3**, and **4** are isoelectronic with respect to the chelate ring π electrons. The structural characteristics in the diazoketiminato complex of palladium(II) has been attributed to the delocalisation in the ligand backbone. Analogous delocalisation has been stated as the origin of several unusual properties in the complexes of 2-((arylamido)phenylazo)pyridines [4]. Among the delocalised azo ligands, arylazopyridine, arylazoimidazole and arylazooximates have been demonstrated to afford transition metal complexes with interesting structures and properties [5]. Identical number of valance electrons of palladium(II) and gold(III) encouraged us to examine the formation of a diazoketiminato chelate of Au(III).

Herein we describe the syntheses, characterisation and structure of the first diazoketiminato complexes of Au(III). The ligand precursors, 2-(arylazo)anilines, LH_2 (Chart 1), bind the metal as an uninegative anion (LH^-), dissociating an amino proton. In LH_2, H represents amino protons.

Syntheses and characterisation of L^2H_2 and L^3H_2 have also been described here for the first time.

2. Experimental

2.1. Materials

All starting materials were used as received from commercial sources; the solvents were purchased from

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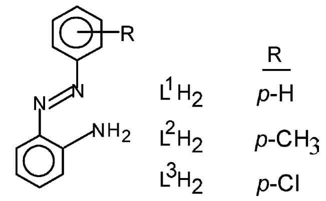


LH_2
5

Chart 1.

E. Marck, Kolkata, India, and purified and dried by reported procedures [6]. *o*-Phenylenediamine, nitrobenzene, *p*-methyl and *p*-chloro nitrobenzene from Loba, Kolkata, India. Tetrachloroauric acid ($HAuCl_4$, XH_2O) from SRL, Kolkata, India. Ethyl alcohol from Bengal Chemical, Kolkata, India. The ligand 2-(phenylazo)aniline (L^1H_2) was prepared following the reported procedure [3].

2.2. Synthesis of ligands

2.2.1. L^2H_2

o-Phenylenediamine (2 g, 18.5 mmol), *p*-methylnitrobenzene (2.5 g, 18.5 mmol) and sodium hydroxide (0.74 g, 18.5 mmol) were mixed and heated at 70 °C with constant scratching for 30 min. The dark pasty mass thus obtained was cooled to room temperature and extracted with benzene. The pure 2-(*p*-tolylazo)aniline, L^2H_2 was obtained by column chromatography on a silica gel (60–120 mesh) column using benzene-petroleum ethere mixed solvent (10/90 v/v) as an eluant. Yield 51%. *Anal.* Found: C 73.95, H 6.20, N 19.92. Calc. for $C_{13}H_{13}N_3$: C 73.93, H 6.16, N 19.90%. ^{1}H NMR ($CDCl_3$): $\delta = 5.81$ (s, NH_2); 6.75 (d, 6H); 6.81 (t, 5H); 7.19 (t, 4H); 7.28 (d, 9H and 11H); 7.74 (d, 8H and 12H); 7.80 (d, 3H); 2.41 (s, *p*-CH_3).

2.2.2. L^3H_2

2-(*p*-Chlorophenylazo)aniline (L^3H_2) was prepared following a similar procedure as described for 2-(*p*-tolylazo)aniline using *p*-chloronitrobenzene in place of *p*-methylnitrobenzene. Yield 7 1%. *Anal.* Found: C 62.25, H 4.39, N 18.19. Calc. for $C_{12}H_{10}N_3Cl$: C 62.20, H 4.32, N 18.14%. ^{1}H NMR ($CDCl_3$): $\delta = 5.73$ (s, NH_2); 6.60 (d, 6H); 6.66 (t, 5H); 7.06 (t, 4H); 7.28 (d, 9H and 11H); 7.62 (d, 8H and 12H); 7.67 (d, 3H).

2.3. Synthesis of complexes

The complexes (L^1H)$AuCl_2$, (L^2H)$AuCl_2$ and (L^3H)$AuCl_2$ were prepared by the reaction of $HAuCl_4$ with L^1H_2, L^2H_2 and L^3H_2, respectively, in ethanol. The details are given below.

2.3.1. $(L^1H)AuCl_2$

An ethanolic solution (20 cm^3) of L^1H_2 (0.13 g, 0.677 mmol) was added to an aqueous solution (20 cm^3) of $HAuCl_4$ (0.23 g, 0.677 mmol). The colour of the solution turned pink. The resulting pink solution was stirred for 3 h, filtered off and washed with distilled water several times. A pure compound was obtained by recrystallisation from dichloromethane. Yield 80%. *Anal.* Found: C 31.05, H 2.25, N 9.03. Calc. for $C_{12}H_{10}N_3AuCl_2$: C 31.03, H 2.20, N 9.00 %. ^{1}H NMR ($CDCl_3$): = 7.61 (s, NH); 6.84 (t, 5H); 6.96 (d, 6H); 7.43–7.55 (m, 9H 11H 12H 8H and 4H); 7.72 (d, 3H).

2.3.2. $(L^2H)AuCl_2$

This complex was prepared following a similar procedure as described for (L^1H)$AuCl_2$ using ligand L^2H_2 in place of L^1H_2. Yield 75%, *Anal.* Found: C 32.70, H 2.59, N 8.80. Calc. for $C_{13}H_{12}N_3AuCl_2$: C 32.64, H 2.51, N 8.79 %. ^{1}H NMR ($CDCl_3$): = 6.85 (t, 5H); 6.96 (d, 6H); 7.25 (d, 9H and 11H); 7.46–7.50 (m, 8H 12H and 4H); 7.71 (d, 3H); 2.43 (s, *p*-CH_3).

2.3.3. $(L^3H)AuCl_2$

This complex was prepared following a similar procedure as described for (L^1H)$AuCl_2$ using ligand L^3H_2 in place of L^1H_2. Yield 72%, *Anal.* Found: C 28.90, H 1.90, N 8.50. Calc. for $C_{12}H_9N_3AuCl_3$: C 28.89, H 1.81, N 8.43 %. ^{1}H NMR ($CDCl_3$): = 7.56 (s, NH); 6.77 (t, 5H); 6.88 (d, 6H); 7.34–7.42 (m; 8H, 12H, 9H, and 11H); 7.47 (t, 4H); 7.63 (d, 3H).

2.4. Physical measurements

Microanalysis (C,H,N) were performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer 783 spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Simadzu UV 1601 spectrophotometer. ^{1}H NMR spectra were obtained on Brucker Avance DPX 300 and Brucker Avance DPX 400 NMR spectrometers in $CDCl_3$ using TMS as the internal standard.

2.5. Crystallography

Single crystals of (L^1H)$AuCl_2$ were grown by slow evaporation of dichloromethane solution at 298K. The size of the crystal suitable for X-ray studies was $0.32 \times 0.26 \times 0.20$ mm^3. Cell parameters were determined by least square fits of 25 machine centered reflections ($2\theta = 15$–$28°$). Data were collected by the ω- scan technique on a Nicolet R 3m/v diffractometer with Mo Kα radiation monochromated by graphite crystal. Absorption correction was not done. Crystal data were collected in Table 1. The structure solution was done by direct methods with the SHELXS 90 pro-

Table 1
Crystallographic data for $(L^1H)AuCl_2$

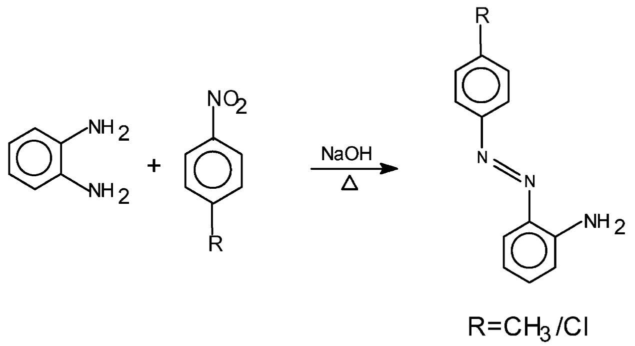
Chemical formula	$C_{12}H_{10}N_3AuCl_2$
Formula weight	464.10
Crystal System	monoclinic
Space group	$P2_1/n$
a (Å)	9.553(4)
b (Å)	8.386(4)
c (Å)	16.978(7)
β (°)	102.05(3)
V (Å^3)	1330.2(10)
Z	4
Temperature (K)	293
λ (Å)	0.71073
ρ_{calcd} (M g/m^3)	2.317
μ (mm^{-1})	11.445
Reflections collected	2445
Independent reflections	2265
R_{int}	0.0518
$R_1(I > 2\sigma)$	0.0482
$wR_2(I > 2\sigma)$	0.1066
GOF[a]	1.075

[a] The goodness-of-fit is defined as $\{W(|F_o| - |F_c|)^2/(n_o - n_v)\}^{1/2}$ where n_o and n_v denote the numbers of data and variables, respectively.

gram. Full matrix least square refinements were performed using the SHELX 97 program (PC version). All non hydrogen atoms were refined anisotopically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions.

3. Results and discussion

The ligands L^2H_2 and L^3H_2 have been synthesised in one pot by the reaction of *o*-phenylenediamine with *p*-methylnitrobenzene and *p*-chloronitrobenzene, respectively, in presence of the sodium hydroxide at elevated temperature (Eq. (1)). Synthesis of L^1H_2 has been described earlier [3].



(1)

The reaction of equimolar LH_2 ligand and tetrachloroauric acid in ethanol affords a dark coloured solid of composition $(LH)AuCl_2$. The complexes are non-conducting, diamagnetic and soluble in common organic solvents giving a pink solution. The analytical data (C,H,N) match well with the composition.

The ligands and complexes display characteristic UV–Vis spectra. The transitions in the visible region (~420 nm) for the ligands are assigned for n → π* and the higher energy transitions (UV-region) for π → π*. The spectra of the metal complexes are distinctly different to that of the ligands. The absorption ~500 nm has been assigned as a metal to ligand charge transfer (MLCT) transition. Representative spectra of the ligand (L^1H_2) and the corresponding complex $((L^1H)AuCl_2)$ have been shown in Fig. 1. The UV–Vis spectral data are collected in Table 2.

The IR spectra of LH_2 exhibit a couple of closely spaced absorptions in the range 3360–3458 cm^{-1}characteristic of ν_{NH2} [7], on the contrary, for $(LH)AuCl_2$ a single band appeared in the range 3257–3320 cm^{-1} characteristic for ν_{NH}. This supports the dissociation of an amino proton from LH_2 upon complex formation and is consistent with ^1H NMR and X-ray data (vide infra). The red shift of $\nu_{N=N}$ (in the range 1337–1353 cm^{-1}) in $(LH)AuCl_2$ compared to LH_2 (1458–1474 cm^{-1}) indicates the coordination of the azo nitrogen [5a,5h–5k]. The absorption near 1610 cm^{-1} in $(LH)AuCl_2$ has been assigned for $\nu_{C=N}$ which are absent in LH_2. The selected IR data are listed in Table 2.

The ligands and complexes display well resolved ^1H NMR spectra. The broad amino proton resonances for $(L^1H)AuCl_2$ and $(L^3H)AuCl_2$ appear in the aromatic region (7.61 and 7.56 ppm, respectively) for the one equivalent proton. In contrast for the L^1H_2 and L^3H_2, the amino protons resonate at 5.90 and 5.73 ppm, respectively, for the two equivalent protons. This is consistent with the dissociation of an amino proton from the ligands (L^1H_2 and L^3H_2) upon coordination. For $(L^2H)AuCl_2$ the same signal is probably obscured by other aromatic proton resonances in the range 7.46–7.50 ppm, however, the amino protons of L^2H_2 have been observed at 5.81 ppm for two the equivalent protons. In the ^1H NMR spectra of the ligands (LH_2), 6H and 4H appear in the range 6.60–6.75 ppm and 7.06–7.20 ppm, respectively, whereas for the complexes ($(LH)AuCl_2$) the

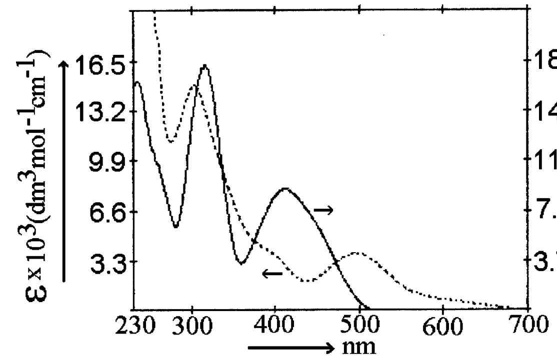


Fig. 1. UV–Vis spectra of L^1H_2 (– –) and $(L^1H)AuCl_2$ (------). The arrows indicate scales of the corresponding spectrum.

Table 2
UV–Vis[a] and IR[b] spectral data

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})	ν/cm^{-1}				
		ν_{NH_2}	ν_{NH}	$\nu_{C=N}$	$\nu_{N=N}$	ν_{Au-Cl}
L^1H_2	416 (8963), 313 (14,455), 243 (14,791)	3456, 3382			1461	
L^2H_2	421 (2668), 321 (5260), 271 (8787)	3458, 3378			1458	
L^3H_2	421 (11,768), 320 (36,693), 233 (28,770)	3432, 3360			1474	
$(L^1H)AuCl_2$	499 (2656), 380[c] (2755), 304 (8787)		3257	1601	1337	334, 273
$(L^2H)AuCl_2$	501 (10,436), 400[c] (11,155), 305 (30,432)		3320	1616	1353	302, 291
$(L^3H)AuCl_2$	501 (3496), 385[c] (3561), 304 (10860)		3311	1617	1342	300, 287

[a] In dichloromethane.
[b] In KBr disc.
[c] Shoulder.

same resonances are downfield shifted and observed within 6.88–6.96 ppm and 7.43–7.50 ppm, respectively. The numbering scheme for the ^{1}H NMR analysis has been followed as shown in Fig. 2.

The crystal structure of $(L^1H)AuCl_2$ has been determined by X-ray crystallography at 293K. A perspective view of the molecule with the atom numbering scheme is shown in Fig. 2. Selected bond distances and angles have been summarised in Table 3.

The gross geometry about Au(III) is square planar, coordinated by the bidentate (N,N) ligand and two chlorides satisfying the tetracoordination. The planar geometry about gold is consistent with its trivalency and the binding of anionic $(LH)^-$ can be inferred since the complex is nonconducting. This is also in accordance with the IR and ^{1}H NMR results (vide supra).

In the six membered chelate ring, the N(1)–C(1) length (1.35(2) Å) is considerably shorter than the C–N single bond length (N(3)–C(7); 1.44(2) Å) in the same molecule. The phenyl ring (C(1), C(2)···C(6)) is distorted with four long (~1.41 Å) and two short bonds (~1.32 Å). The C(2)–N(2) length (1.37(2) Å) is also considerably shorter than the C–N single bond length which is expected to occur as a result of delocalisation and formation of diazoketiminato chelate, **7**.

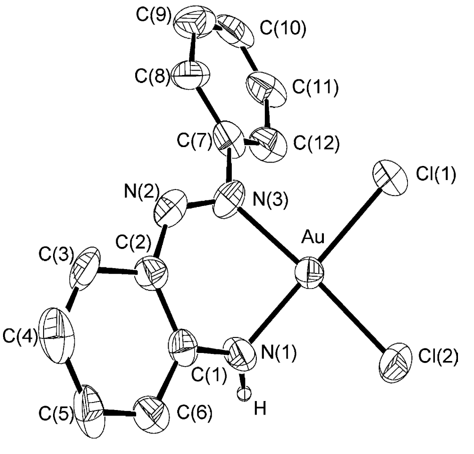
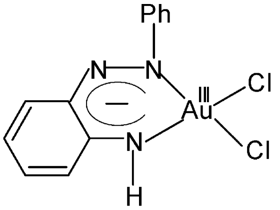


Fig. 2. ORTEP plot of $(L^1H)AuCl_2$ with atom-numbering scheme. Hydrogen atoms, except that on N(1), are omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for $(L^1H)AuCl_2$

Distances			
Au–N(1)	1.973(12)	Au–N(3)	2.044(11)
Au–Cl(1)	2.308(4)	Au–Cl(2)	2.289(4)
N(1)–C(1)	1.35(2)	N(2)–N(3)	1.27(2)
N(2)–C(2)	1.37(2)	N(3)–C(7)	1.44(2)
C(1)–C(2)	1.42(2)	C(1)–C(6)	1.40(2)
C(2)–C(3)	1.43(2)	C(3)–C(4)	1.32(2)
C(4)–C(5)	1.38(3)	C(5)–C(6)	1.33(2)
Angles			
N(1)–Au–N(3)	86.4(5)	N(3)–Au–Cl(1)	93.5(4)
Cl(1)–Au–Cl(2)	90.6(2)	Cl(2)–Au–N(1)	89.5(4)
C(1)–N(1)–Au	120.5(10)	N(1)–C(1)–C(2)	121.5(14)
C(1)–C(2)–N(2)	123.8(14)	C(2)–N(2)–N(3)	124.8(12)
N(2)–N(3)–Au	123.5(10)	N(1)–Au–Cl(1)	178.0(4)



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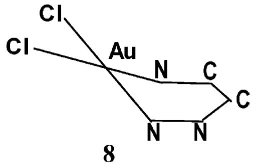
In the square planar complex Cl(1) and Cl(2) are *trans* to N(1) and N(3), respectively, where the Au–Cl(1) distance (2.308(4) Å) is longer than Au–Cl(2) (2.289(4) Å) due to the stronger *trans* influence of the imino nitrogen (N(1)) than the azo nitrogen (N(3)).

The fragment containing N(1), N(3), Au, Cl(1) and Cl(2) is planar with a mean deviation 0.01 Å. On the other hand the fragment containing N(1), C(1), C(2), N(2), and N(3) is also satisfactorily planar (mean deviation 0.03 Å). The dihedral angle between these two planes, 38.6°, is in accordance with the boat structure of the chelate ring, **8**.



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4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 198808. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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References

[1] (a) F. Hartl, T.L. Snoeck, D.J. Stufkens, A.B.P. Lever, Inorg. Chem. 34 (1995) 3887;
(b) H. Masui, A.B.P. Lever, E.S. Dodsworth, Inorg. Chem. 32 (1993) 258;
(c) A. Vogler, H. Kunkely, Angew Chem. Int. Ed. Engl. 19 (1980) 221;
(d) A.S. Attia, S. Bhattacharya, C.G. Pierpont, Inorg. Chem. 34 (1995) 4427;
(e) C.G. Pierpont, C.W. Lange, Progr. Inorg. Chem. 41 (1994) 331;
(f) T. Hirao, Coord. Chem. Rev. 226 (2002) 81.

[2] (a) G. Aromi, P. Gamez, O. Roubeau, P.C. Berzal, H. Kooijman, A.L. Spek, W.L. Driessen, J. Reedijk, Inorg. Chem. 41 (2002) 3673;
(b) F. Wang, X. Wu, A.A. Pinkerton, P. Kumaradhas, D.C. Neckers, Inorg. Chem. 40 (2001) 6000;
(c) F.A. Chavez, J.A. Briones, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 38 (1999) 1603;
(d) A. Cingolani, Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B.W. Skelton, A.H. White, Inorg. Chem. 41 (2002) 1151;
(e) J. Barbera, A. Elduque, R. Gimenez, F.J. Lahoz, J.A. Lopez, L.A. Oro, J.L. Serrano, B. Villacampa, J. Villalba, Inorg. Chem. 38 (1999) 3085;
(f) T.-Y. Chen, J. Vaissermann, P. Doppelt, Inorg. Chem. 40 (2001) 6167;
(g) J.R. Bradbury, J.L. Hampton, D.P. Martone, A.W. Maverick, Inorg. Chem. 28 (1989) 2392, and references therein;
(h) H.K. Shin, M.J. Hampden-Smith, T.T. Kodas, A.L. Rheingold, J. Chem. Soc., Chem. Commun. (1992) 217, and references therein;
(i) Y. Ohtsuka, D. Miyazaki, T. Ikeno, T. Yamada, Chem. Lett. (2002) 24;
(j) L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031, and references therein.

[3] N. Maiti, S. Pal, S. Chattopadhyay, Inorg. Chem. 40 (2001) 2204.

[4] (a) C. Das, S.-M. Peng, G.-H. Lee, S. Goswami, New J. Chem. 26 (2002) 222;
(b) A. Saha, P. Majumdar, S.-M. Peng, S. Goswami, Eur. J. Inorg. Chem. (2000) 2631;
(c) A. Saha, P. Majumdar, S. Goswami, J. Chem. Soc., Dalton Trans. (2000) 1703.

[5] (a) P.K. Santara, D. Das, T.K. Misra, R. Roy, C. Sinha, S.-M. Peng, Polyhedron 18 (1999) 1909;
(b) P. Majumder, S.-M. Peng, S. Goswami, J. Chem. Soc., Dalton Trans. (1998) 1569;
(c) B.K. Santra, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (1997) 1883;
(d) N. Bag, G.K. Lahiri, A. Chakravorty, Inorg. Chem. 31 (1992) 40;
(e) B.K. Ghosh, A. Chakravorty, Coord. Chem. Rev. 95 (1989) 239;
(f) D. Dutta, A. Chakravorty, Inorg. Chem. 22 (1983) 1085;
(g) I. Chakraborty, S. Bhattacharyya, S. Banerjee, B.K. Dirghangi, A. Chakravorty, J. Chem. Soc., Dalton Trans. (1999) 3747;
(h) T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672;
(i) D. Das, C. Sinha, Transition Metal Chem. 23 (1998) 517;
(j) T.K. Misra, C. Sinha, Transition Metal Chem. 23 (1998) 171;
(k) T.K. Misra, D. Das, C. Sinha, Polyhedron 16 (1997) 1463;
(l) D. Das, M.K. Nayak, C. Sinha, Transition Metal Chem. 22 (1997) 172;
(m) C.K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, Inorg. Chem. 33 (1994) 6140;
(n) C.K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, Inorg. Chem. 35 (1996) 2442.

[6] (a) P. Chattopadhyay, M.K. Nayak, S.P. Bhattacharya, C. Sinha, Polyhedron 16 (1997) 1291;
(b) F. Basuli, P. Chattopadhyay, C. Sinha, Polyhedron 15 (1996) 2439.

[7] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Part B), fifth ed., 1997.