

SHORT COMMUNICATIONS

COORDINATION COMPLEXES OF A TETRADENTATE N₄ MACROCYCLIC LIGAND b,h-BIS(DINITRO BENZO)1,4,7,10 CYCLO TETRADECANE WITH Cu(II), Ni(II) AND Co(II)

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In continuation of our earlier work on macrocyclic complexes of first row transition metals¹⁻⁴, the present paper deals with the synthesis of some hexacoordinated complexes of a new N₄ macrocyclic ligand with Cu(II), Ni(II) and Co(II). The complexes have been assigned octahedral structures on the basis of analytical, magnetic and spectral studies with anions coordinated in the trans-axial positions.

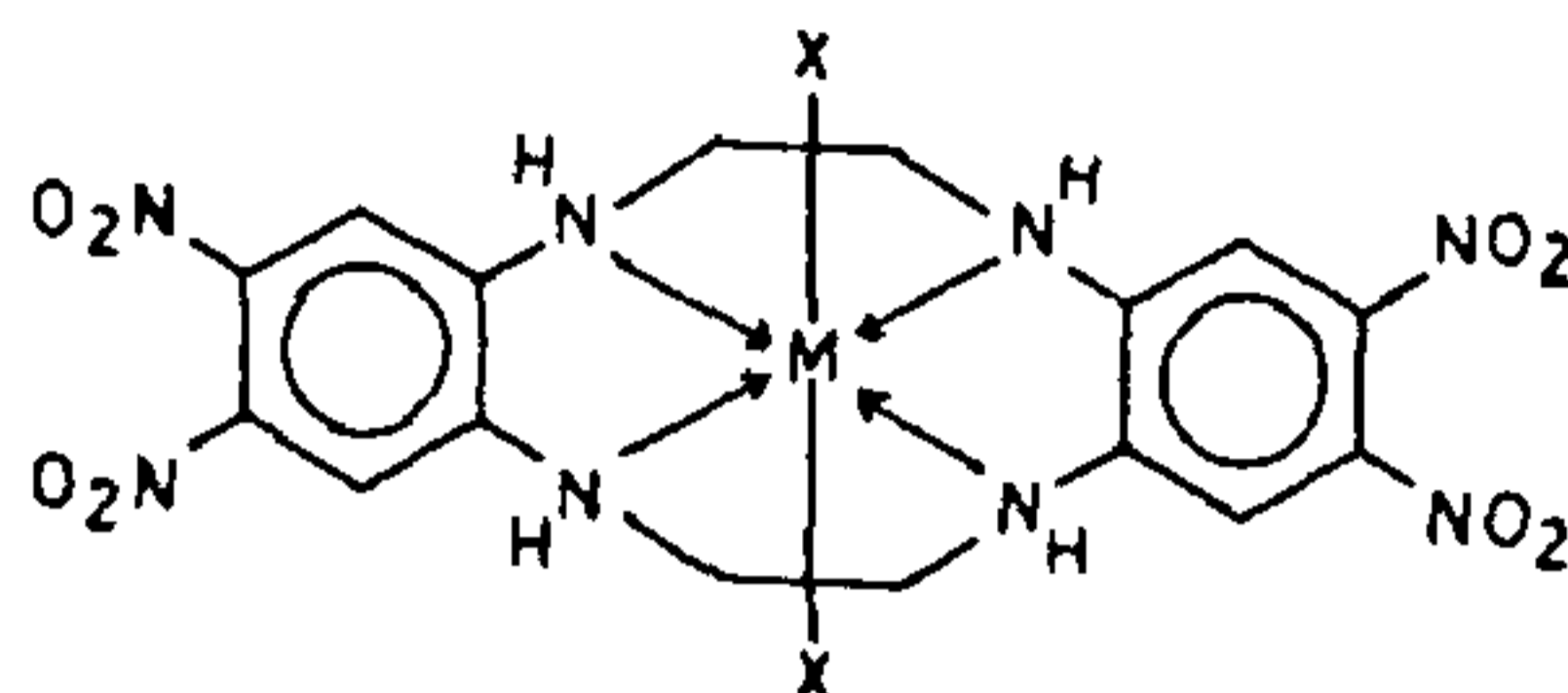
The complexes have been prepared in two steps— (i) 0.01 M of the appropriate metal salt in methanol was refluxed with an excess of ethylenediamine (0.04 M) for about 10 h and (ii) to this solution, 1,2-dichloro 4,5-dinitrobenzene prepared by the nitration of 1,2-dichlorobenzene was added and the solution was further refluxed for 5 h. The complexes were crystallized and purified by running over TLC plates, dried and analysed.

The conductivity of the complexes was measured in methanol by direct reading conductivity bridge, the analytical and the IR studies were obtained from CDRI, Lucknow and the electronic and magnetic studies were conducted at the Guru Nanak Dev University, Amritsar.

The analytical data of complexes (table 1) correspond to 1:1 stoichiometry while the molar conductance values are in the usual range of non-electrolytes and thus the molecular formulae of the

complexes are $[M(L)X_2]$ where $X = Cl^-$, SCN^- or ClO_4^- .

The ligand is a tetradentate macrocyclic as the two nitro groups on the ring render both chloro groups labile and hence result in their condensation with two moles of ethylenediamine in the presence of metal salt giving the following skeletal structure.



It is a 12-membered macrocycle and is slightly undersized for a regular square planar structure and hence an octahedral structure is attained instead by the trans-axial coordination of anions. The coordination of the ligand is confirmed by a lowering of the ν_{NH} frequency to 3300 cm^{-1} in the complexes^{5,6}, while the nitro group vibrations seen at 1428 and 1320 cm^{-1} correspond to uncoordinated values^{7,8}. The bands corresponding to N-bonded thiocyanate are seen at 2080 and 810 cm^{-1} , and those due to weakly coordinating perchlorate^{9,12} at 1150 and 1190 cm^{-1} .

The Cu(II) complexes possess magnetic moments around 1.90 BM and show one broad band in electronic spectra around 16.50 kK with a shoulder on each side. The Ni(II) complexes have magnetic moments in the range 3.00–3.15 BM and the electronic spectra show two bands in the region 14–19 kK and the third band around 25 kK. These resemble the spectral features of $NiLX_2$ complexes.

Table 1 Analytical and molar conductance data

Complex	% Found (Calc.)				Molar conductance in MeOH ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
	M	C	H	N	
Cu(L)(ClO ₄) ₂	9.82 (8.93)	27.65 (27.02)	2.62 (2.25)	15.18 (15.76)	24.26
Cu(L)(SCN) ₂	10.54 (10.11)	33.90 (34.42)	2.41 (2.54)	22.62 (22.33)	32.29
Ni(L)(SCN) ₂	8.86 (9.42)	34.92 (34.69)	2.93 (2.57)	22.62 (22.48)	21.82
Ni(L)(ClO ₄) ₂	8.80 (8.32)	26.85 (27.21)	2.75 (2.28)	15.82 (15.87)	27.63
Co(L)Cl ₂	10.52 (10.19)	33.45 (33.22)	2.66 (2.77)	19.62 (19.38)	28.32
Co(L)(SCN) ₂	9.24 (8.78)	27.32 (27.19)	2.21 (2.26)	15.26 (15.86)	27.48

The Co(II) complexes possess magnetic moment values in the range 5.0–5.2 BM. The electronic spectra show a multiplet band structure in the region 16–19 kK corresponding to pseudooctahedral geometry.

The above evidence confirms the octahedral geometry for the complexes as a consequence of mismatch in the ring causing distortion from square planar structure. The large values of Dq suggest the ligand field around the metal is quite strong as expected.

One of the authors (NA) is grateful to CSIR, New Delhi for a fellowship.

2 September 1987; Revised 13 November 1987

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INTERTRAPPEAN DINOSAURIAN FOSSILS FROM ANJAR AREA, KACHCHH DISTRICT, GUJARAT

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DINOSAURIAN fossils have been recorded for the first time from intertrappean cherty, splintery limestone and grey shale forming bed No. 3 from a locality about 3.5 km south of Anjar town, near eastern margin of 0.90 in toposheet 41 I/4 (figure 1).

Mesozoic sediments comprising of sandstone and fossiliferous shale with plant fossils of Upper Gondwana affinity¹, belonging to Bhuj Formation, are exposed to the west of Anjar town. These sediments underlie Deccan lava flows having four intertrappean beds and resemble interstratified volcano sedimentary sequence², reported from western Kachchh. The basal two intertrappean beds are unfossiliferous. The third intertrappean bed is about 8.5 m thick and comprises dark grey, green and chocolate-coloured gypseous shale, lenses of fossiliferous banded chert and cherty and splintery limestone rich in dinosaurian bones, invertebrate assemblage including *Physa*, *Paludina*, *Lymnea* and plant fossils.

Occurrence of intertrappean and late Upper Cretaceous dinosaurs is known from many parts of the world including India³. Indian occurrences include Dayapar⁴ in Kachchh, Rahioli⁵ and adjacent areas^{6,7} in Kheda district in western India and Dongargaon⁸, Pisdura⁹, Takli¹⁰, Ada, Mudimial¹¹ areas, Jabalpur in central India⁸ and southern India^{12,13}.

Dinosaurian fossils

The present find of dinosaurian fossils includes parts of limb bones viz. tibia, fibula, radius, ulna and femur (figure 2b), scapula (figure 2a), ribs (figure 2c), vertebrae (figure 2d), claws (figure 2e), coprolites and ossified skin (figure 2f). The dinosaurian remains are very fragile, but well-preserved. They were presumably buried in the ponds surrounded by thick bushes of creepers and ferns.

The femur bone (figure 2b) is 80 cm long and shows features for attachments of trochanteric muscle, and articular surface¹⁴. Ribs include cervical type (figure 2c), which are typically straight as compared to arched ribs. The associated vertebrae are opisthocoelous and are dorsal type (figure 2d). The claws¹⁵ resemble those of allosaurid described from central India⁸. Some of the teeth resemble those of Megalosaurid³. The scapula has affinity towards sauropod⁴.

The fauna indicates a possible habitation of sauropod and theropod (Megalosaurid) dinosaurs in the area. Evidences of a violent central type of eruption in the vicinity of their habitat have been recognized¹⁶, which may have led to their extinction in this area.

The intertrappean beds at Dayapar have been assigned uppermost Cretaceous to Lower Palaeocene age^{17,18}. The Anjar intertrappean bed