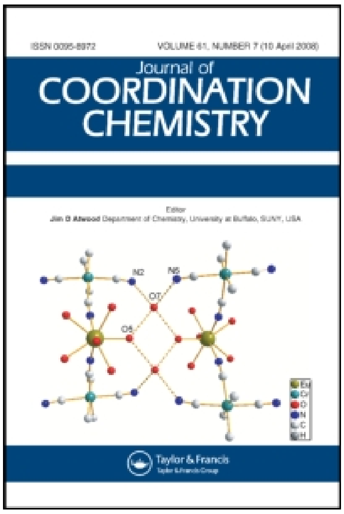


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

NOTE: STRUCTURE OF A COPPER(II) COMPLEX WITH THE MACROCYCLIC LIGAND HEXACYCLEN

Mariana I. Mitewa[a]; Panayot R. Bontchev[a]; Daniella R. Vassileva[a]; Konstantin S. Kabassanov[b]; Ekaterina N. Zhecheva[c]; Dimiter R. Mechandjiev[c]
[a] Departmentt of Chemistry, University of Sofia, Sofia, Bulgaria [b] Institure of Solid State Physics, Bulgariam Academy of Science, Safia, Bulgaria [c] Institure of General and Inorganic Chenistry, Bulgarian Academy of Sciences, Safia, Bulgaria

To cite this Article Mitewa, Mariana I. , Bontchev, Panayot R. , Vassileva, Daniella R. , Kabassanov, Konstantin S. , Zhecheva, Ekaterina N. and Mechandjiev, Dimiter R.(1988) 'NOTE: STRUCTURE OF A COPPER(II) COMPLEX WITH THE MACROCYCLIC LIGAND HEXACYCLEN', Journal of Coordination Chemistry, 17: 3, 287 — 290

To link to this Article: DOI: 10.1080/00958978808070779

URL: http://dx.doi.org/10.1080/00958978808070779

J. Coord. Chem. 1988, Vol. 17, pp. 287–290
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

STRUCTURE OF A COPPER(II) COMPLEX WITH THE MACROCYCLIC LIGAND HEXACYCLEN

MARIANA I. MITEWA, PANAYOT R. BONTCHEV*,
DANIELLA R. VASSILEVA

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria.

KONSTANTIN S. KABASSANOV

Institute of Solid State Physics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

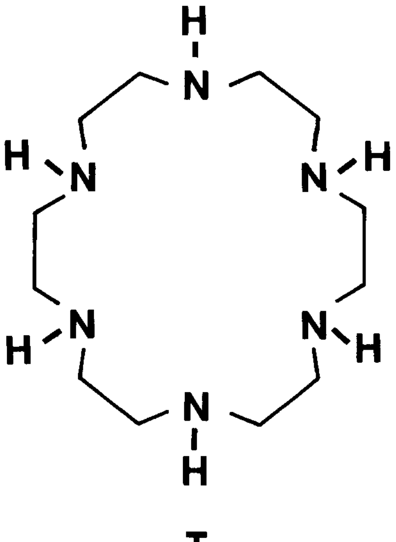
EKATERINA N. ZHECHEVA and DIMITER R. MECHANDJIEV

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

(Received August 12, 1987; in final form October 22, 1987)

Keywords: Copper, hexacyclen, magnetochemistry, esr, structure

The saturated macrocyclic ligand 1,4,7,10,13,16-hexaazaoctadecane (hexacyclen, **I**) exhibits excellent coordination ability[1-5] and extraction properties[6,7] towards different metal ions. Due to the remarkable flexibility of the ligand complexes with different structures are formed.[1-5]



I

---

* Author for correspondence

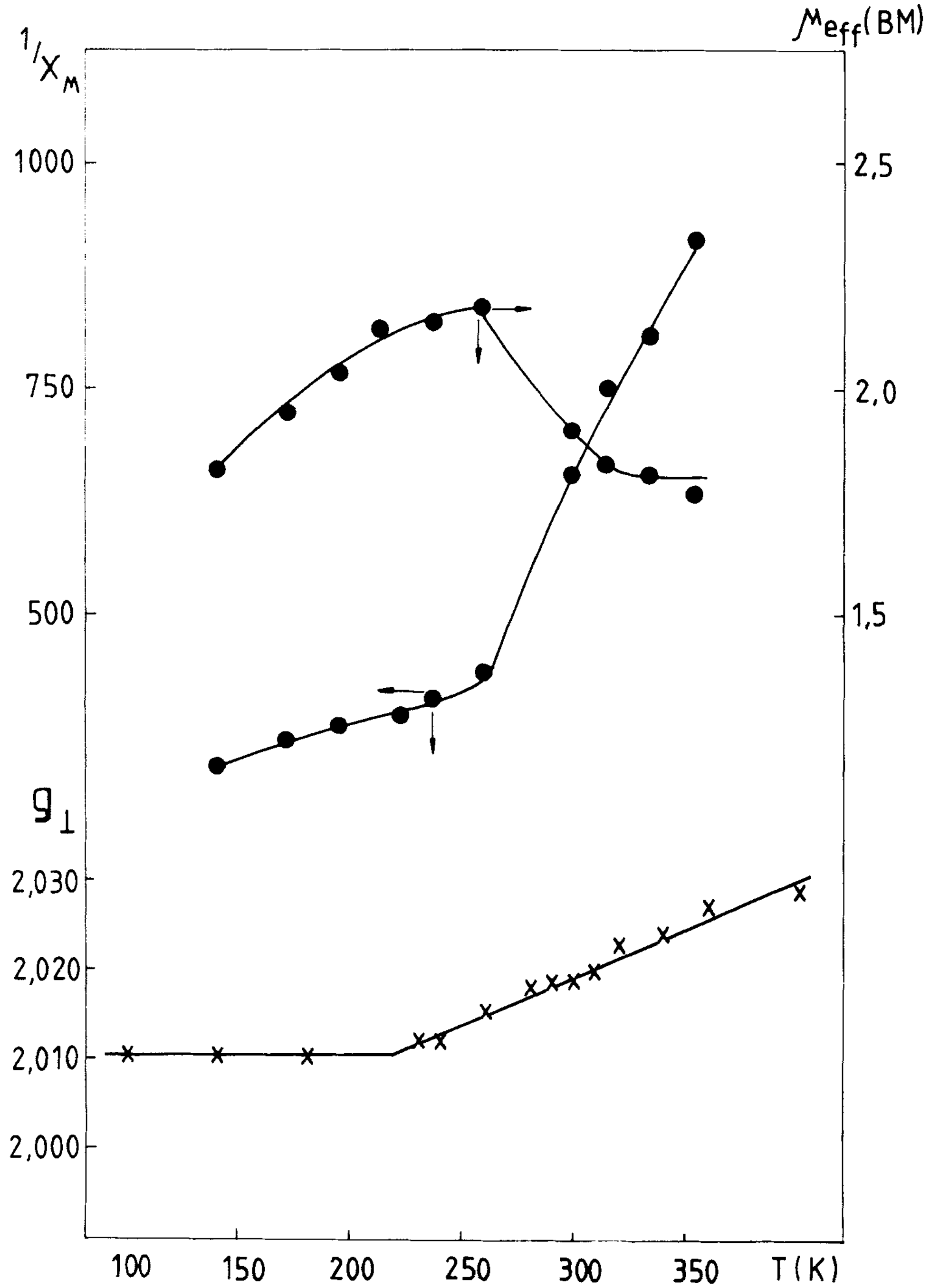


FIGURE 1 Temperature dependence of reciprocal magnetic susceptibility ($1/\chi_m$), magnetic moment (μ_{eff}) and $g_{\perp}$-values of Cu(Hex).2TPB.

Only few data are reported concerning the structure of the Cu(II)-hexacyclen complex. On the basis of electronic and EPR spectral data alone, it was concluded[1,3] that its structure is a constrained octahedral one, as $g_{\parallel} > g_{\perp}$. This ratio, however, is typical for Cu(II) complexes of rhombic symmetry (c.n. 4) with slightly misaligned tetragonal axes.[8] For that reason the aim of the present work was to provide a more detailed investigation on the structure of Cu(Hex).2TPB (TPB ≡ tetraphenylborate) by means of EPR and magnetochemical measurements.

EXPERIMENTAL

The Cu(Hex).2TPB complex was obtained as described elsewhere.[1,4,5] Hexacyclen.$3H_2SO_4$ (Aldrich) used as initial starting material. All other reagents used were of AR grade.

IR spectra were obtained on a Perkin Elmer 580 instrument (KBr-disks). EPR spectra were measured using an X-band EPR spectrometer (ERS-220, GDR) equipped with a thermostat thus allowing spectra to be recorded at fixed temperatures in the range 90–370 K. Magnetic susceptibility measurements were measured over the temperature range 130–350 K in an argon atmosphere according to the Faraday method.

RESULTS AND DISCUSSION

The temperature dependences of magnetic susceptibility ($1/\chi_M$) and effective magnetic moment (μ_{eff}) in the range 130–350 K are represented in Fig. 1. It is evident that these dependences are anomalous, changing their character at 240 to 250 K. Up to 230 K the temperature dependence of μ_{eff} is typical of a tetrahedral structure.[9] The magnetochemical data show that at temperatures higher than 250 K the structure of the Cu(Hex).2TPB complex is octahedral—μ_{eff} at ambient temperatures (1.95 BM) and its temperature-dependence is typical of such a structure.[9]

In order to obtain additional structural information EPR spectra of a polycrystalline sample of the complex were studied at different temperatures in the range 90–370 K. As has been reported[3] the EPR spectrum of the complex is anisotropic with $g_{\parallel} = 2.220 \pm 0.001, g_{\perp} = 2.010 \pm 0.001, A_{\parallel} = 120$ Oe. The temperature dependence of the anisotropic components was followed and the data obtained are represented in Table I and Fig. 1.

It is evident that up to 230–240 K the EPR parameters are temperature independent, while at higher temperatures $g_{\perp}$ increases. Similar temperature dependences of g-parameters have been interpreted as being due to static and dynamic Jahn–Teller distortions of the complex.[10-12]

The data obtained indicate a temperature-dependent structure. At lower temperatures the structure of Cu(Hex).2TPB is a distorted tetrahedral one; the g-values observed are typical for rhombic symmetry with slightly misaligned tetragonal axes,[8] i.e., of a compressed tetrahedron. In this case only four nitrogen atoms of the N_6-macrocycle are coordinated to Cu(II). At higher temperatures a distorted octahedral coordination is realized. Evidently, the increase of the bond lengths favours the coordination of all nitrogen atoms of the ligand, to form a constrained octahedron. This conclusion is in agreement with the fact that three different NH vibrations are observed in the IR spectrum of the complex (at 3300, 3260 and 3220 cm^{-1}). A similar structure has been proved by means of X-ray diffraction for a Cu(II) complex with an N_6-macrocyclic ligand analogous to hexacyclen.[13]

TABLE I
EPR parameters for Cu(Hex).2TPB.

T K	g * ± 0.0001	$g_{\_}$ ± 0.001	A * ± 2/Oe
93	2.220	2.010	120
133	2.220	2.010	122
173	2.216	2.010	124
223	2.216	2.012	120
233	2.215	2.012	120
253		2.016	
263		2.016	
273		2.018	
283		2.019	
293		2.019	
303		2.020	
313		2.023	
333		2.024	
353		2.027	
373		2.029	

* Due to line-broadening the determination of g and A was impossible at higher temperatures than those indicated.

REFERENCES

1. R.W. Hay, B. Jeragh, S.F. Lincoln and G.H. Searle, *Inorg. Nucl. Chem. Lett.*, **14**, 435 (1978).
2. A. Bencini, L. Fabrizzi and A. Poggi, *Inorg. Chem.*, **20**, 2544 (1981).
3. K. Miyoshi, H. Tanaka, E. Kimura, S. Tsuboyama, S. Murata, H. Shimizu and K. Ishizu, *Inorg. Chim. Acta*, **78**, 23 (1983).
4. M. Mitewa, P.R. Bontchev, E. Zhecheva, D. Mechandjiev, K. Kabassanov and D. Vassileva, *Proc. 11th Conf. Coord. Chem.*, Smolenice, ČSSR, 1987, p. 235.
5. M. Mitewa, P.R. Bontchev, E. Zhecheva, D. Mechandjiev, K. Kabassanov and D. Vassileva, *Inorg. Chim. Acta*, **134**, 17 (1987).
6. P. Fux, J. Lagrange and P. Lagrange, *J. Chim. Phys.*, **81**, 321 (1984).
7. S. Arpadjan, M. Mitewa and P.R. Bontchev, *Talanta*, **34**, 953 (1987).
8. B. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
9. B.N. Figgis and J. Lewis, *Progress in Inorganic Chemistry*, (John Wiley, New York, 1964) vol. 6.
10. J. Pradilla-Sorzano and J.P. Fackler, Jr., *Inorg. Chem.*, **12**, 1182 (1973).
11. B. Hathaway, M. Duggan, A. Murphy, J. Mullane, C. Power, A. Walsh and B. Walsh, *Coord. Chem. Rev.*, **36**, 267 (1981).
12. E. Paap, W.L. Driessen, J. Reedjik, M. Dartmann and B. Krebs, *Inorg. Chim. Acta*, **121**, 185 (1986).
13. G.R. Newkome, V.K. Magestic and F.R. Fronczek, *Inorg. Chim. Acta*, **77**, L47 (1983).