

A STUDY OF SOME TRANSITION METAL COMPLEXES WITH HEXADENTATE NNNNOO-CHROMOPHORIC TYPE LIGANDS

Mohamed A. Khalifa
Chemistry Department, Faculty of Science, Alexandria University,
Alexandria, Egypt

(Received June 9, 1988; revised March 15, 1989)

ABSTRACT. The synthesis and characterization of chromium, cobalt, nickel and copper complexes with hexadentate ligands 1,9-diamino-3,7-diazanonane-3, 7-diacetic acid and triethylenetetraamine N^2, N^3 -diacetic acid (2,3,2-Tet-DA and TTDA respectively) are reported. The ligands and their cyclic amide precursors were characterized by ^{13}C NMR and IR spectroscopy. The bonding and electronic structures of the isolated complexes were investigated. *trans* and *cis* geometrical isomers of $[Co(2,3,2-Tet-DA)]^+$ were synthesised and characterized. The electronic states of the new complexes are discussed.

INTRODUCTION

One of the most recently developed aspects of metal ion complexes is the utilization of multidentate ligands as complexing agents. The hexadentate EDTA is probably the most versatile of all ligands, forming the tetranegative NNOOOO-type complexes, often very stable with most metal ions (1,2). It has found many analytical and practical applications based on the stability of its metal complexes and, consequently, its ability to bind or sequester the metal ions. On the other hand, relatively little attention has been paid to the coordination chemistry of the dinegative hexadentate NNNNOO-chromophoric ligands. They have an advantage over the NNOOOO-type ligands since they have 4 nitrogen donor atoms and the complexes are generally more stable with ligands having strongly basic donor atoms. Moreover, there is complete charge neutralization for these NNNNOO-ligands upon complexation with divalent metal ions. For M^{3+} ions, stable cationic, $[M^{III}(N_4O_2)]^+$, complexes are formed in contrast to the anionic $[M^{III}(N_2O_4)]^-$ complexes.

In this paper the synthesis and reactions of the dinegative NNNNOO-hexadentate type ligands with some transition metal ions are reported. Attempts are made to gain further information about (i) the coordination modes of these ligands, (ii) the stereochemistry of their metal chelates, and (iii) the correlation between the stereochemistry of these metal chelates and their electronic spectra.

EXPERIMENTAL

Visible absorption spectra were measured in 1 cm quartz cells at 25°C using a Cary 14 recording spectrophotometer with a tungsten lamp. IR spectra were measured on a Perkin-Elmer model 621 and model 283 spectrophotometer using KBr discs and/or as Nujol mulls. ^{13}C NMR spectra were recorded on a JEOL JNM-FX60 FT NMR spectrometer. The spectra were obtained at 15 MHz in D_2O with benzene as external standard. Satisfactory elemental analyses data were obtained for all new compounds.

Syntheses of the Complexes

Piperazinone. Diethylamine (30 ml) was mixed with ethylenediaminemonoacetic acid ethylester, C_2H_5EDMA in purified benzene (500 ml). The precipitated diethylamine hydrochloride was filtered off and the filtrate was allowed to stand at ambient temperature for about 40 hr. The crystalline product was filtered off and dried *in vacuo*.

2,3,2-Tet-DA.4HCl. A mixture of piperazinone (0.20 mol), 1,3-dibromopropane (0.16 mol) and anhydrous sodium carbonate (0.20 mol) in 225 ml of pure ethanol was refluxed for 24 hr. The mixture was filtered to remove unreacted sodium carbonate and the filtrate was concentrated to about 50 ml and then cooled in an ice-bath. A white solid (assumed to be 4,4'-propanobis-(2-piperazinone)) was separated by filtration and then refluxed in 40 ml of 6N HCl for 4 hr. The solution was concentrated using a rotary evaporator, and the white product was separated by filtration.

TTDA.4HCl. The procedure described for the preparation of 2,3,2-Tet-DA.4HCl was followed using 1,2-dibromoethane instead of 1,3-dibromopropane. The 4,4'-ethanobis(2-piperazinone) was refluxed for 2 hr in 6N HCl. The solution was concentrated and the white product isolated.

[Ni(TTDA)]. The pH of a solution of TTDA.4HCl (0.01 mol) in water (20 ml), was adjusted to 7.00 with 3N NaOH and added to a solution of Ni(II) acetate tetrahydrate (0.01 mol) in water (10 ml). The mixture was refluxed for 4 hr. The complex was precipitated by the addition of ethanol (10 ml), filtered off, washed with hot ethanol and then dried *in vacuo*.

[Cu(TTDA)]H₂O. A solution of TTDA.4HCl (0.01 mol) in water (20 ml), was added to a solution of copper(II) acetate (0.01 mol) in water (10 ml), and the pH of the mixture was adjusted to 5.50 by the addition of 3N aq. NaOH. The reaction mixture was refluxed for 3 hr. The complex was precipitated by addition of methanol (15 ml), filtered off, washed with hot methanol, and dried *in vacuo*. This complex has also been prepared at pH = 7.00, substituting copper nitrate for copper acetate. The formula of the hydrate was determined by heating 0.600 g of the complex at 100°C until it reached a constant weight of 0.5700 g. The weight loss was attributed to water which is driven off during heating.

[Cr(TTDA)]Cl. A single piece of granulated zinc (3) was added to a solution of chromium trichloride hexahydrate (0.01 mol) in water (20 ml). To this mixture a solution of TTDA.4HCl (0.01 mol) in water (20 ml) was added and the pH adjusted to 4.5 by the addition of 3N aq. NaOH. The mixture was refluxed for 5 hr, filtered and concentrated to about 20 ml. The product which crystallized on cooling, was washed with water and then dried *in vacuo*.

[Co(2,3,2-Tet-DA)](OAC). A solution of 2,3,2-Tet-DA.4HCl (0.01 mol) in water (20 ml) was added to a solution of cobalt(II) acetate tetrahydrate (0.01 mol) in water (10 ml). The pH was adjusted to 6.2 (using aq. 3N NaOH). The solution was warmed for 15 minutes, followed by the dropwise addition of 1.5 ml of 30% H₂O₂. The reaction mixture was refluxed on a steam bath for 2 hr, air oxidized and concentrated. A purple-red complex separated out upon addition of 10 ml ethanol. The precipitated complex was filtered off, washed with hot ethanol, and then dried *in vacuo*.

Trans- and cis geometrical isomers of [Co(2,3,2-Tet-DA)]Cl. [Co(2,3,2)-Tet-DA](OAC) (0.50 g) was dissolved in the minimum amount of water (2 ml) and the resulting purple-red solution (3 ml) was then introduced into a 2.5 cm x 30 cm column containing Dowex 50 W-X8 (200-400 mesh) cation exchange resin in the K⁺ form. The column was then eluted with 0.01 M KCl solution (0.5 ml/min). Three coloured bands, deep pink, purple-red, and pale pink, were obtained. The purple-red (major) band was strongly bound to the column and was separated after the elution of the first band by elution with 0.05 M KCl. The pale pink (minor) band was very strongly bound to the column and separated

by elution with saturated KCl solution. The second purple-red eluate was evaporated under an air stream to near dryness and the purple-red crystals were separated, washed with ethanol and air-dried. This complex was identified by means of its electronic absorption spectrum as *trans*[Co(2,3,2-Tet-DA)]Cl as discussed later. The first eluate was concentrated by means of an air stream and characterized by its electronic spectrum as *cis*-[Co(2,3,2-Tet-DA)]Cl.

RESULTS AND DISCUSSION

Infrared Spectra. The positions of the most important IR bands are listed in Table 1. Asymmetric carboxylate stretching frequencies have been established as criteria for distinguishing between protonated carboxylate groups (1700–1750 cm^{-1}) and carboxylate groups which are coordinated to metal ions (1600–1650 cm^{-1}) in metal aminopolycarboxylic acid complexes (4–6). Table 1 shows that all hexadentate complexes with TTDA and 2,3,2-Tet-DA show only one very strong band in the 1600–1650 cm^{-1} indicating that the carboxylate groups are coordinated.

Table 1. Infrared asymmetric N-H and C=O stretching frequencies.

Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$
$\text{C}_2\text{H}_5\text{EDMA}$	3425	1735
Piperazinone	3238, 3160, 3030	1650
4,4'-ethanobis(2-piperazinone)	3190, 3060	1650
4,4'-propanobis(2-piperazinone)	3160, 3095	1645
TTDA	3350	1720
2,3,2-Tet-DA	3350	1720
Co(2,3,2-Tet-DA)Cl	3200	1638
Ni(TTDA)	3230	1625
Cu(TTDA)·H ₂ O	3225	1620
Cr(TTDA)Cl	3220	1625

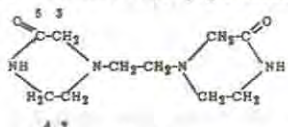
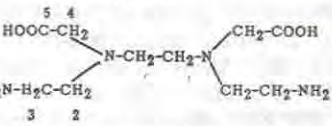
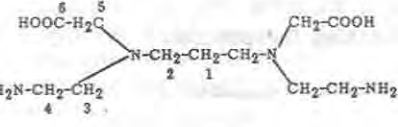
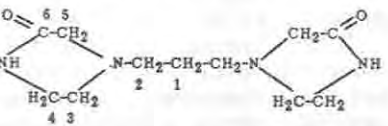
^{13}C NMR spectra. Table 2 summarizes the results of the ^{13}C NMR measurements of the two new ligands investigated and their cyclic amides. From the five peaks observed in the methylene region for each of 4,4'-propanobis(2-piperazinone) and 2,3,2-Tet-DA, the two peaks at 40.91 and 23.54 ppm in case of 4,4'-propanobis(2-piperazinone), and the two at 34.25 and 22.40 for 2,3,2-Tet-DA represent the two nonequivalent carbon atoms of trimethylenediamine -

$\text{>N-CH}_2\text{-CH}_2\text{-CH}_2\text{N}<$ (carbons 2 and 1, Table 2). The lower field resonance can be assigned to the terminal carbon atoms (2), and the higher field resonance is assigned to the middle carbon (1). Such assignment is in close agreement with the chemical shifts observed for similar carbon atoms in a number of cobalt(III) and nickel(II) complexes (7). Although the assignments of peaks in the methylene region is somewhat ambiguous, the absence of this highest field resonance in the spectra of 4,4'-ethanobis(2-piperazinone) and TTDA, and the presence of only four peaks in the methylene region for each, is consistent with the suggested structures for both 4,4'-propanobis(2-piperazinone) and 2,3,2-Tet-DA.

Electronic absorption spectra

Cobalt(III) complexes. The three possible geometrical isomers of [Co(2,3,2-Tet-

Table 2. ^{13}C Median chemical shifts and tentative assignments for TTDA, 2,3,2,-Tet-DA and their cyclic amides

Compounds	Chemical Shift(ppm)	Assignment
4,4'-ethanobis(2-piperazinone)	40.52	C-1
	48.32	C-2
	53.35	C-4
	55.79	C-3
	171.97	C-5
TTDA	36.29	C-1
	52.22	C-2
	53.52	C-3
	56.12	C-4
	171.28	C-5
4,4'-propanobis(2-piperazinone)	23.54	C-1
	40.91	C-2
	48.37	C-3
	55.19	C-4
	56.00	C-5
	172.07	C-6
2,3,2-Tet-DA	22.40	C-1
	34.25	C-2
	37.82	C-3
	55.19	C-4
	58.11	C-5
	171.58	C-6

DA)]⁺ are shown in Fig. 1. The visible absorption spectrum of the octahedral [Co(2,3,2-Tet-DA)]Cl isolated from the second purple-red eluate shows two bands at 18.1 (100) and 27.2 (120) μK corresponding to the $A_{1g} + T_{1g}$ and $A_{1g} + T_{2g}$ transitions of an octahedral complex (8). In addition the spectrum shows a shoulder on the higher energy side of the first absorption band. It is well known experimentally (9, 10) and theoretically (11,12) that the *trans*-[Co(N₄O₂)] type complexes exhibit a large splitting in the first absorption band. Whereas for the *cis*-[Co(N₄O₂)] type complexes, this band is nearly symmetrical. Therefore it is clear that Co(2,3,2-Tet-DA)]Cl has *trans* configuration. If only coordinated atoms are considered, these complexes have tetragonal symmetry (13). The $T_{1g}(O_h)$ level is split into two levels with $A_2(D_{4h})$ and $E(D_{4h})$ symmetry (14,15). In the present complex there is a weaker field along the unique axis (O-O) than in the

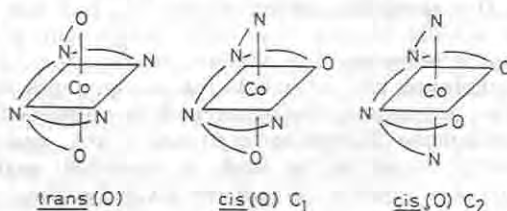


Fig. 1 The three geometrical isomers for [Co(2,3,2-Tet-DA)]⁺.

plane perpendicular to it; therefore it is predicted that the $E(D_{4h})$ level will be lower in energy than the $A_2(D_{4h})$ level. Consequently a major component at 18.1 κK is assigned to be $E(D_{4h})$ and the shoulder at about 22.0 κK is assigned to be $A_2(D_{4h})$.

The spectrum of the deep pink crystals isolated from the first eluate displays two bands at 26.9 κK and 19.0 κK , with no evidence for the splitting in the low energy transition. This strongly suggests that the complex is the *cis*-[Co(2,3,2,-Tet-DA)]⁺ geometrical isomer (9-12).

Chromium(III) complexes. The absorption spectrum of [Cr(TTDA)]Cl complex shows two bands at 19.0 and 26.0 κK . Their shapes suggest that this complex has pseudo-octahedral symmetry. The Cr(III) ion (d^3) has a ground state in a strong O_h field, (t_{2g})³. In O_h symmetry the lower energy spin-allowed band for Cr(III) is ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and the one at higher energy is ${}^4A_{2g} \rightarrow {}^4T_{1g}$.

Nickel(II) complexes. The Orgel diagram for Ni(II) d^8 in octahedral field indicates that the spectra of octahedral Ni(II) complexes exhibit three bands due to the three spin-allowed transitions; ν_1 ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2 ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; ν_3 ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (14,16-21). In addition, two spin-forbidden bands due to ${}^3A_{2g} \rightarrow {}^1E_g(D)$ and ${}^3A_{2g} \rightarrow {}^1E_g(G)$ are frequently observed (14,20).

Table 3. The Electronic Spectral Data of Ni(TTDA) Chelate

Medium	Band Maxima κK ($\epsilon 1. \text{ mol}^{-1} \text{ cm}^{-1}$)			
	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ν_3	${}^3A_{2g} \rightarrow {}^3T_{1g}$ ν_2	${}^3A_{2g} \rightarrow {}^1E_g$	${}^3A_{2g} \rightarrow {}^3T_{2g}$ ν_1
H ₂ O	27.02(6.33)	17.24(4.32)	15.38(sh), 12.90(2.20), 10.81(sh)	10.30(9.33), 9.70(bsh)
CH ₃ OH	27.02(7.94)	17.24(5.58)	15.50(sh), 12.82(2.06), 10.87(sh)	10.24(10.07), 9.80(bsh)
DMSO	27.02(15.29)	16.94(4.70)	14.92(sh), 12.50(2.81), 10.30(sh)	10.00(10.38), 9.61(bsh)

sh: shoulder

bsh: broad shoulder

The spectra of Ni(TTDA) in Table 3 and Figs. 1 and 2 confirm the octahedral arrangement around the nickel(II) ion. Most probably this complex belongs to C_2 or to a group of lower symmetry. No definite splitting of absorption bands, however, can be attributed to such low symmetry, and the tentative assignments given in Table 3 are made on the assumption that the effective symmetry is O_h .

The ν_1 band at about 10.00 κK (${}^3A_{2g} \rightarrow {}^3T_{2g}$) in the spectra of Ni(TTDA) is quite broad, suggesting a small splitting caused by lower symmetry. The presence of weak bands or shoulders on the low energy side of ν_2 and the high energy side of ν_1 probably correspond to spin-forbidden transitions from the triplet ground state to singlet levels $1D$ and $1G$. The ν_3 band in the spectra of Ni(TTDA) in DMSO is hidden by charge-transfer absorption.

Copper(II) complexes. The electronic spectrum of Cu(TTDA).H₂O exhibit a broad band centered at 15.03 κK , with two well-developed shoulders on the higher (ca. 17.20 κK) and lower energy sides (ca. 13.50 κK). The energy level diagram arising from the 2D spectroscopic term of the free copper(II) ion in the ligand field symmetry D_{4h} would predict three transitions, while that for C_2 or even lower

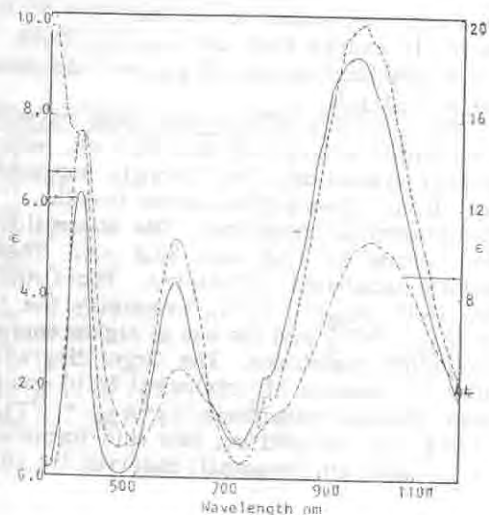


Fig. 2 Absorption spectra of Ni(TTDA) chelate in water (—) and in methanol (---) solutions, left-hand scale; and in dimethyl-sulfoxide solution (- · - · -) right-hand scale.

symmetry would require four transitions. The poor band resolution observed in the spectrum of the $\text{Cu}(\text{TTDA})\cdot\text{H}_2\text{O}$ complex suggests that the splitting of the E_g level in going from D_{4h} symmetry to lower symmetry is not large. Accordingly, D_{4h} symmetry can be used for this copper(II) chelate (22).

The precise order of the energy levels in D_{4h} symmetry is uncertain (23-25). The splitting of the ${}^2E_g(\text{O}_h)$ level will be greater than that of the ${}^2T_{2g}(\text{O}_h)$ level and the ${}^2B_{2g}$ level will always lie below the ${}^2E_g(D_{4h})$ level. As the transition ${}^2B_{1g} \rightarrow {}^2E_g$ is likely to be the most intense transition (26) the presence of a relatively less intense shoulder on the higher energy side implies the sequence: ${}^2B_{1g} < {}^2B_{2g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$ in this complex. Accordingly, the most intense band at 15.03 κK may tentatively be assigned to the ${}^2B_{1g} \rightarrow {}^2E_g$ transition, while the shoulder at 17.20 κK is due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$. The ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition appears as a shoulder at 13.50 κK .

ACKNOWLEDGEMENTS

Helpful discussions with Prof. Dr. M.F. Iskander, Dr. S.S. Massoud and Dr. N.J. Less - Gayed are gratefully acknowledged.

REFERENCES

1. R. Pribil "Analytical Applications of EDTA and Related Compounds", Pergamon, New York (1972).
2. G.D. Christian "Analytical Chemistry", 3rd ed., John Wiley, New York (1980).
3. K. Wieghardt, P. Chaudhuri, B. Number and J. Weiss, *Inorg. Chem.*, **21**, 3086 (1982).
4. D.H. Busch and J.C. Bailar, *J. Am. Chem. Soc.*, **75**, 4574 (1953); *J. Am. Chem. Soc.*, **78**, 716 (1956).
5. M.L. Morris and D.H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

6. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York (1963).
7. M.A. Khalifa, Ph.D. Dissertation, Wayne State University, Michigan, USA (1981).
8. L.E. Orgel, *J. Chem. Soc.*, 4756 (1952).
9. M. Linhard and M. Wegel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951).
10. M. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **40**, 1868 (1967).
11. C.J. Ballhausen and C.K. Jorgensen, *K. Dan. Vidensk. Selsk., Mat-Fys. Medd.*, **29**, 14 (1955).
12. H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).
13. F.A. Cotton "Chemical Applications of Group Theory", 2nd ed., Wiley-Interscience, Chap. 9, New York (1971).
14. R.A. Wentworth and T.S. Piper, *Inorg. Chem.*, **4**, 709 (1965).
15. J.I. Legg and D.W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).
16. A.D. Liehr and C.J. Ballhausen, *Ann. Phys.*, **6**, 134 (1957).
17. C.J. Ballhausen, *Rev. Trav. Chim.*, **75**, 665 (1956).
18. O. Bostrup and C.K. Jorgensen, *Acta. Chem. Scan.*, **11**, 1223 (1957).
19. O.G. Holms and D.S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
20. C.K. Jorgensen, *Act. Chem. Scand.*, **9**, 1362 (1962).
21. D.M. Goodgame and L.M. Venazi, *J. Chem. Soc.*, **616**, (1963).
22. J.M. Proceter, B.J. Hathaway and P. Nicholls, *J. Chem. Soc.*, (A), 1678 (1968).
23. R.L. Belford, M. Calvin and Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
24. D.W. Smith, *Inorg. Chem.*, **5**, 2236 (1966).
25. M.G. Clark and R.G. Burns, *J. Chem. Soc.*, (A), 1034 (1967).
26. B.N. Figgis, "Introduction to Ligand Fields", Interscience, New York pp. 208 (1966).