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Copper(II), Cobalt(II), Nickel(II) and Iron(III) Complexes of some N,N,N′,N′-tetrakis[(2-benz[d]imidazolyl)methyl] alkanediamines

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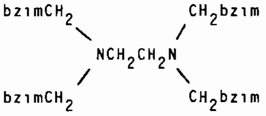
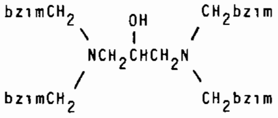
Copper(II), cobalt(II), nickel(II) and iron(III) complexes of N,N,N′,N′-tetrakis[(2-benz[d]imidazolyl)methyl]alkanediamines, where alkanediamine denotes 1,2-ethanediamine, 1,2-propanediamine, 2-hydroxy-1,3-propanediamine or n-butanediamine, have been isolated. Each metal ion takes a variety of configurations for the non-rigid binding sites offered by these pliable ligand: Cu(II) lies in a distorted tetragonal geometry, Co(II) in a tetrahedral one, and Ni(II) and Fe(III) is an octahedral or a tetrahedral one.

Metal ion-substitution of metalloproteins in place of the inherent metal ions has been evaluated as one of the most elegant and effective ways to investigate the structure of their active sites, since it is generally accompanied by the least denaturation of the parent proteins. However, attention has to be paid if the incoming metal ion is to be introduced into the original metal site, if the incorporated metal ion is ligated by the original groups, and if the steric configuration of the incorporated metal ion properly reflects that of the original metal ion. In spite of these problems the metal ion-substitution has afforded beneficial information in the examination of the active sites of various metalloproteins [1]. In all cases familiar complexes of low molecular weight and specially-designed model compounds have facilitated the interpretation of the spectral properties of the active site of metalloproteins.

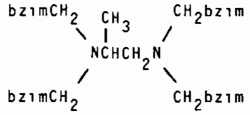
We are interested in the stereochemical trends of metal ions such as Cu(II), Co(II), Ni(II) and Fe(III) lying at the active site of proteins, and have undertaken the study of model systems involving simple ligands of low molecular weight. Some N,N,N′,N′–tetrakis[(2-benz[d]imidazolyl)methyl] alkanediamines were chosen as ligands, since the ligands of this type have received increasing attention as one of the most useful compounds to simulate active sites of metalloproteins [2].



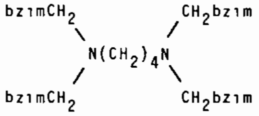
TBED



TBPO



TBID



TBBD

Experimental

Preparations

The free ligand TBED was synthesized as described in the literature [3], and TBID, TBPO and TBBD from corresponding diamines, chloroacetic acid and *o*-phenylenediamine according to the usual methods [4]. *Anal.* Calcd for $C_{35}H_{34}N_{10}$ (TBID): C, 69.35; H, 6.29; N, 21.86%. Found: C, 69.16; H, 6.26; N, 21.86%. Calcd for $C_{35}H_{34}N_{10}O\cdot 4.5H_2O$ (TBPO): C, 60.75; H, 6.28; N, 20.25%. Found: C. 60.83; H, 6.28; N, 20.06%. Calcd for $C_{36}H_{36}N\cdot 2.5H_2O\cdot 2C_2H_5OH$ (TBBD): C, 64.40; H, 7.16; N, 18.78%. Found: C, 64.74; H, 7.11; N, 18.71%. Metal complexes were prepared by mixing each metal ion and ligand in a ratio of 1:1 or 2:1 in methanol, and allowing the mixture to stand at room temperature or at 4 °C in a refrigerator. Complexes isolated are tabulated in Table I, with analytical data.

Spectral Measurements

Infrared spectra were measured by employing the KBr-disk method with a Hitachi 260-10 grating infrared spectrometer. Ultraviolet, visible and near-infrared spectra were obtained on a Hitachi 323 spectrometer at room temperature using a 1-cm path length quartz cell. ESR spectra at X-band frequencies were measured with a JEOL JES-FE1X spectrometer as dimethylsulfoxide glass at 77K. MCD spectra were measured by a JASCO MOE-1 spectropolarimeter equipped with an electromagnet of 1.06 T.

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TABLE I Analytical Data of Isolated Complexes

Complex	Obsd (%)			Calcd (%)		
	C	H	N	C	H	N
$Cu(TBED)(ClO_4)_2 \cdot 0.5H_2O$	47.92	3.73	16.44	47.92	3.90	16.44
$Cu_2(TBED)Cl_4 \cdot 3H_2O \cdot 2CH_3OH$	45.60	4.65	14.58	45.51	4.88	14.75
$Cu_2(TBED)(NO_3)_4 \cdot 1.5H_2O \cdot CH_3OH$	41.27	3.58	19.22	41.37	3.87	19.33
$Cu(TBID)(ClO_4)_2$	49.13	4.00	16.62	49.04	4.00	16.34
$Cu_2(TBID)Cl_4$	48.37	4.19	15.92	48.17	4.19	16.05
$Cu_2(TBPO)(NO_3)_4 \cdot 4H_2O$	39.78	3.85	18.74	39.74	4.00	18.54
$Cu_2(TBPO)Cl_4 \cdot 5H_2O$	43.45	4.28	14.35	43.35	4.57	14.45
$Cu_2(TBBD)(ClO_4)_4 \cdot 3H_2O$	36.23	3.55	12.06	36.40	3.56	11.80
$Co(TBED)Cl_2 \cdot H_2O$	55.81	4.58	18.90	56.05	4.70	19.23
$Co_2(TBED)Cl_4 \cdot 3H_2O$	45.89	4.59	15.22	45.65	4.28	15.66
$Co(TBID)Cl_2 \cdot 2.5H_2O$	54.86	4.95	18.22	54.62	5.11	18.20
$Co_2(TBID)Cl_4$	49.13	4.03	16.17	49.20	4.01	16.40
$Co_2(TBPO)Cl_4$	48.01	4.17	16.52	48.29	3.94	16.10
$Co_2(TBBD)Cl_4 \cdot 3CH_3OH$	48.07	4.80	14.07	47.76	4.93	14.29
$Ni(TBED)Cl_2 \cdot 3.5H_2O \cdot CH_3OH$	52.26	5.21	17.54	52.19	5.38	17.40
$Ni_2(TBED)Cl_4 \cdot 3H_2O \cdot 3CH_3OH$	44.84	4.76	14.08	44.88	5.09	14.15
$Ni(TBID)Cl_2 \cdot 2.5H_2O$	54.56	4.94	18.36	54.64	5.11	18.21
$Ni(TBPO)Cl_2 \cdot 4H_2O$	51.54	5.09	17.20	51.74	5.21	17.25
$Ni_2(TBBD)Cl_4 \cdot 4.5H_2O$ (blue)	45.30	4.47	14.70	45.56	4.78	14.76
$Ni_2(TBBD)Cl_4 \cdot 9H_2O$ (green)	41.81	5.12	13.65	41.97	5.28	13.60
$Fe_2(TBED)Cl_6 \cdot 7H_2O$	39.62	4.48	13.58	39.60	4.50	13.58
$Fe_2(TBID)Cl_6 \cdot 2H_2O$	44.17	4.30	14.54	44.01	4.01	14.67
$Fe_2(TBPO)Cl_5 \cdot 5.5H_2O^a$	42.10	4.20	14.30	42.13	4.45	14.04
$Fe_2(TBBD)Cl_6 \cdot 3H_2O \cdot 2CH_3OH$	43.48	4.44	13.25	43.41	4.79	13.25

[a] Cl·Obsd 17.52%, Calcd 17.76%.

Results and Discussion

Copper(II) Complexes

Two types of copper(II) complexes of TBED, $Cu(TBED)X_2$ (X: ClO_4^-) and $Cu_2(TBED)X_4$ (X: Cl^-, NO_3^-), were obtained, despite the use of 2:1 Cu(II): TBED for each preparation. The mononuclear complex displayed a rhombic ESR spectrum, having g-values of g_1 2.29, g_2 2.10, g_3 2.01, and A values of A_1 13.1 mK and A_3 5.4 mK [3]. The high rhombic character, which is somewhat similar to those of plantacyanin [5], mavicyanin [6] and rusticyanin [7], probably stems from an unusual steric configuration of a distorted square-pyramid [3, 8]. $Cu_2(TBED)$ exhibited ESR signals of Cu(TBED) and free Cu^{II} ($g_{\parallel}$ 2.43, $A_{\parallel}$ 11.2 mK), as previously noted by Birker *et al.* [8]. Apparently a quite rapid decomposition may occur in the parent binuclear complex. The absorption spectrum of the chloride complex (measured as nujol mull) in contrast to its DMSO solution exhibited no appreciable d–d transition in the visible region, while d–d absorption of the nitrate complex appeared at the same wavelength both for the crystal and for the DMSO solution. The delicate difference in the mode of coordination can be realized by the high flexibility of the TBED-ligand. Absorption spectrum of $Cu(TBED)(ClO_4)_2$ showed the d–d transitions at 710 and 1020 nm, being characteristic of square-pyramidal geometry (Fig. 1) [9]. On the other hand, absorption spectra of $Cu_2(TBED)Cl_4$ clearly indicate the presence of Cu(TBED) and another copper(II) complex containing a peak at around 900 nm.

Complexes of TBID, an analogue of TBED, displayed similar spectra, supporting the above interpretation. ESR analysis of $Cu(TBID)(ClO_4)_2$ has also revealed the rhombic character of g_1 2.29, g_2 2.10, g_3 2.01, A_1 13.3 mK and A_3 5.2 mK. $Cu_2(TBID)Cl_4$ also exhibited two species, Cu(TBID) and free Cu(II). In addition, the absorption spectrum of $Cu_2(TBID)Cl_4$ also indicated the presence of two species quite similar to the case of TBED (Table II). The shoulders at *ca.* 300 nm for both $Cu_2(TBED)Cl_4$ and $Cu_2(TBID)Cl_4$ (not shown) can be attributed to the binding of chloride ion with Cu(II), whereas mononuclear perchlorate complexes do not exhibit the shoulder.

As for the structure of the binuclear complexes $Cu_2(TBPO)X_4$ (X: ClO_4^-, Cl^-, NO_3^-), the hydroxy group of TBPO are not dissociated and are free from coordination. Their ESR spectra were prominent in appreciably broad 7-hyperfine signals of the Z-principal axis component ($g_{\parallel}$ 2.27, $A_{\parallel}$ 70 G) for $\Delta M_s = 1$ transition. In addition, there appeared a weaker signal

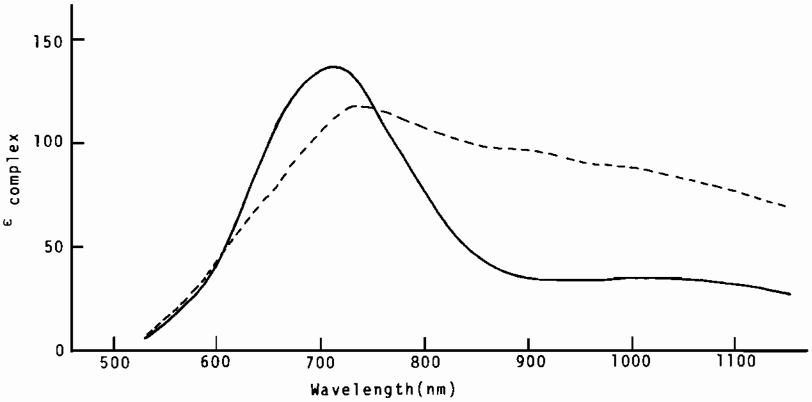

Fig. 1. Absorption spectra of $Cu(TBED)(ClO_4)_2$ (——) and $Cu_2(TBED)Cl_4$ (– – –).

TABLE II Absorption Spectral Data

Complex	$\lambda_{max}(\epsilon_{complex})$
$Cu(TBED)(ClO_4)_2$	705(136) 1000(48)
$Cu_2(TBED)(NO_3)_4$	715(163) 980(63)
$Cu_2(TBED)Cl_4$	725(116) 900(96) 1000(88)
$Cu(TBID)(ClO_4)_2$	697(139) 1000(46)
$Cu_2(TBID)Cl_4$	725(165) 915(137) 1000_{sh}
$Cu_2(TBPO)(NO_3)_4$	790(137)
$Cu_2(TBPO)Cl_4$	740(205)
$Cu_2(TBBD)(ClO_4)_2$	685(230)
$Co(TBED)Cl_2$	460(27) 505(46)
$Co_2(TBED)Cl_4$	450(33) 510(61) 610(85) 665(109)
$Co(TBID)Cl_2$	455(25) 506(37)
$Co_2(TBID)Cl_4$	455(26) 510(52) 600(115) 610(135) 625(141) 665(206)
$Co_2(TBPO)Cl_4$	$550(186)_{broad}$ 890(82) 990(82)
$Co_2(TBBD)Cl_4$	530_{sh} 566(300) 586(327) 616(284)
$Ni(TBED)Cl_2$	360(27) 565(16) 1000(21)
$Ni_2(TBED)Cl_4$	370(48) 594(20) 1050(43)
$Ni(TBID)Cl_2$	369(27) 500_{sh} 579(19) 800_{sh} 980(26)
$Ni(TBPO)Cl_2$	350(15) 510_{sh} 553(12) 790(4) 900(8)
$Ni_2(TBBD)Cl_4$ (blue)	405(27) 560(84) 598(114) 616(100) 900(8)
(green)	410(42) 675(20)
$Fe_2(TBED)Cl_6$	592(226)
$Fe_2(TBID)Cl_6$	596(1963)

due to the $\Delta M_s = 2$ transition at the half-field, indicating that the two copper(II) ions interact with each other mainly by the dipole–dipole interaction mechanism [10]. The d–d absorptions of these complexes were indicative of the usual tetragonal or square-pyramidal copper(II) (Table II) [11].

TBBD-complexes exhibited the similar spectral character with those of TBPO-complexes, except for a weakening of the $\Delta M_s = 2$ ESR signal and a sharpening of the $\Delta M_s = 1$ signal ($g_{\parallel}$ 2.29, $A_{\parallel}$ 70 G) owing to the increase of the intervening methylene chain-length, leading to the separation of Cu–Cu distance.

Cobalt(II) Complexes

The ligand TBED gave 1:1 and 1:2 TBED: Co(II) complexes. However, the formally binuclear complex $Co_2(TBED)Cl_4$ is composed of Co(TBED) and $CoCl_4$ [12], as disclosed by careful inspection of the absorption spectrum (Fig. 2). The former contributes to the bands at 450 and 510 nm, and the latter to those at 610 and 665 nm. In agreement with this, Thompson *et al.* [13] reported that a tripod-like ligand tris(2-benz[d]imidazolyl)amine(TBEA) forms $[Co(TBED)X]_2(CoX_4)$. The magnetic circular dichroism(MCD) spectrum clearly indicated that both Co's are tetrahedral [14]. Thus the aliphatic nitrogen does not seem to be coordinated to Co(II) in Co(TBED), which involves four benz[d]imidazole nitrogens. Supporting the above consideration, TBID offered a quite similar absorption spectrum (Table II).

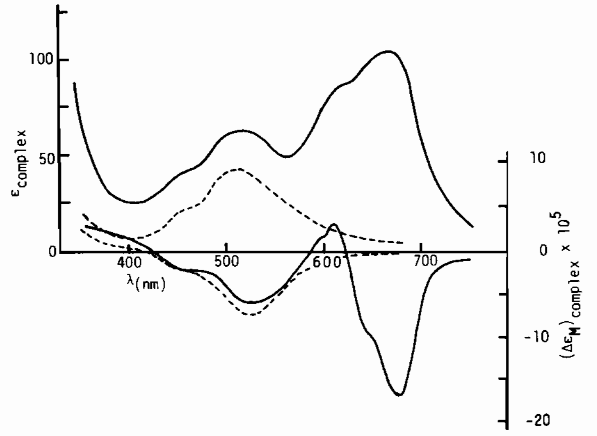

Fig. 2. Absorption and MCD spectra of $Co(TBED)Cl_2$ (– – –) and $Co_2(TBED)Cl_4$ (——).

On the other hand, real binuclear complexes have been isolated for TBPO and TBBD. For these complexes there are no indications of the presence of larger counter ions such as $CoCl_4$. Two benz[d]-imidazole nitrogens and an aliphatic nitrogen are basically able to be coordinated around each cobalt (II) ion, although it is not certain whether or not the latter nitrogen really participates in coordination. Both the complexes are supposed to be tetrahedral, judging from the magnitude of d–d bands in the visible region. Cobalt(II) ions are known to be tetrahedral in most cases when they are substituted for the inherent copper ions at the active site in copper proteins [14].

Nickel(II) Complexes

Ni(TBED), Ni_2(TBED, Ni(TBID), Ni(TBPO) and Ni_2(TBBD) (green form) have been isolated as crystals and all these complexes seem to contain octahedral Ni(II), considering the magnitudes of the d–d bands (Table II). The only exception is Ni_2(TBBD) (blue form), which is crystallized as Ni_2(TBBD)·4.5 H_2O after the isolation of the octahedral green nonahydrate. The coordination geometry of Ni(II) in the blue form is considered to be tetrahedral, since the magnitude of the d–d band is comparatively greater. Ni(II) has been known to exhibit both octahedral and tetrahedral in proteins [15].

Iron(III) Complexes

No 1:1 complex has been isolated for iron and only binuclear complexes have been obtained. Fe_2(TBED)Cl_6 and Fe_2(TBID)Cl_6 unexpectedly exhibited an absorption at *ca.* 600 nm, although their ESR spectra suggested the presence of only high spin Fe(III) species. The fact may indicate that Fe-TBED complex might be composed of two species, one of which would take the tetrahedral geometry, hence the magnitude of forbidden d–d transition might be increased [16]. However, the present band might be due to a charge-transfer transition [17], since the magnitude of the absorption is too strong to be a d–d band.

On the other hand, the TBPO complex shows no prominent band in the visible region, clearly indicating that both Fe(III) ions are in the high spin state and octahedral in their geometries. As is visualized in Fig. 3, the high spin Fe(III) really exists, but a broadened rhombic with g ~ 2 also exists. As the low spin state is usually realized for six-coordinated Fe(III) in a strong ligand field, the signal might originate from interaction of the two high-spin Fe(III) ions. Elemental analysis (Table I) indicated that the hydroxy group of TBPO is dissociated to give the alkoxo group, through which the two Fe(III) ions are bridged. A preliminary experiment revealed that Fe_2^{II}(TBPO) binds molecular oxygen at a low temperature, prior to a sluggish irreversible oxidation of Fe(II) to be Fe(III), which might be related with iron-iron interaction. TBBD afforded only high-spin Fe(III) complex with no apparent d–d interactions.

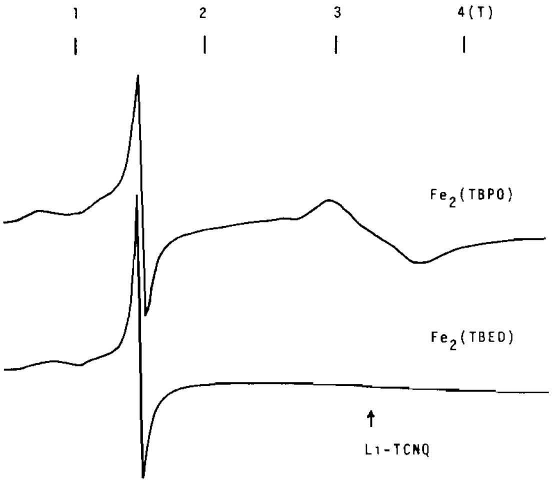

Fig. 3. ESR spectra of Fe_2(TBPO) and Fe_2(TBED) at 77 K and 9.25 GHz.

On account of the non-rigid coordination sites afforded by the present ligands, Cu(II) is incorporated in a slightly strained tetragonal fashion, Co(II) in a tetrahedral one, and Ni(II) and Fe(III) in an octahedral or a tetrahedral one. The variable coordination chemistry of this kind is supposed to be well-related to those ions held by proteins noted hitherto, and hence would help to interpret the spectral characteristics of native and modified metalloproteins.

Acknowledgements

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