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COPPER(II) AND NICKEL(II) COMPLEXES OF A NEUTRAL PENTADENTATE SCHIFF BASE

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Abstract—A new pentadentate Schiff base 2,6,10-triaza-1,11-bis(2′-aminophenyl)-undeca-1,10-diene, *abaDPT*, and its complexes of general formula M(*abaDPT*)X_2 where M = Cu(II), Ni(II), X = Cl, Br, I, NO_3, and ClO_4, have been prepared. The complexes have been characterized by electronic and IR spectra, EPR, magnetic moments, molar conductances, and elemental analysis. IR data show an interaction between halide anion of the outer coordination sphere and the complexed amino group. EPR and spectrophotometric data of most of the copper compounds are consistent with a distorted square pyramidal geometry. Single crystal EPR studies of Cu(*abaDPT*)$(NO_3)_2$ and Cu(*abaDPT*)Br_2 revealed that copper atoms in the former compound occupy two magnetically inequivalent places in the lattice while copper atoms in the latter compound take identical sites. Principal *g* tensor axes of the two compounds have been determined.

Transition metal complexes of Schiff base ligands are of interest since they exhibit a tendency to form various structural types and display a wide variety of magnetic properties. Although numerous linear pentadentate Schiff bases were prepared and investigated in recent years, only a limited number contained a set of five identical donor atoms. Prince and Stotter,[1] Coleman and Taylor,[2] and Simmons *et al.*[3] prepared linear Schiff bases with solely nitrogen donors derived from 2-formylpyridine and polyamines. Copper complexes of some of them functionally resemble hemocyanin in its capacity of reversible binding of oxygen.

Interesting properties of the aforementioned compounds prompted us to study metal complexes with other linear Schiff bases comprising identical sets of donor atoms. Preparative studies in our laboratory have shown that 2-aminobenzaldehyde condenses with bis(3-aminopropyl)amine to give 2,6,10-triaza-1,11-bis(2′-aminophenyl)-undeca-1,10-diene, *abaDPT*, a doubly condensed Schiff base with potentially five donor nitrogen atoms. This paper reports the synthesis and properties of *abaDPT* and its complexes with copper(II) and nickel(II).

EXPERIMENTAL

Bis(3-aminopropyl)amine and 2-nitrobenzaldehyde were obtained from Fluka and were used without further purification. All chemicals and solvents were of reagent grade or equivalent. 2-Aminobenzaldehyde was prepared from 2-nitrobenzaldehyde by the literature method.[4]

2,6,10-*Triaza*-1,11-*bis*(2′-*aminophenyl*)-*undeca*-1,10-*diene*, abaDPT

A solution of freshly prepared 2-aminobenzaldehyde (0.05 mol) and bis(3-aminopropyl)amine (0.025 mol) in benzene (1.5 dm^3) was heated in a flask equipped with a Dean–Stark trap and a reflux condenser. After the stoichiometric quantity of water forming in the reaction was collected in trap, the mixture was concentrated under reduced pressure and the oily residue was extracted several times with hot *n*-hexane. Collected extracts deposited upon cooling the Schiff base which was recrystallized from

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n-hexane to give a white powder of *abaDPT* (30–40% yield).

General preparation of Cu(abaDPT)X_2 (X = Cl, Br, NO_3, ClO_4) *and* Ni(abaDPT)X_2 (X = Cl, Br, I, NO_3, ClO_4) *complexes*

To a hot solution of 5 mmol of the appropriate metal salt in 20 cm^3 of the methanol–water 1:1 mixture (in the case of $CuCl_2$ 10 cm^3 of pure methanol was used) a solution of 5 mmol of *abaDPT* in 20 cm^3 of methanol was added slowly. After 30 min of stirring in room temperature the precipitated complex was filtered off, washed with cold methanol and recrystallized twice from a methanol–water mixture. Crystals of copper complexes were olive-green and those of nickel complexes ranged in colour from green to grey–brown.

Preparation of Cu(abaDPT)I_2

Hot solutions of copper(II) sulphate (0.01 mol in 30 cm^3 of the methanol–water 1:1 mixture) and *abaDPT* (0.01 mol in 20 cm^3 of methanol) were mixed together. To the resulting mixture a solution of barium iodide (0.01 mol in 100 cm^3 of water) was added. After cooling the precipitate was filtered off, washed with cold methanol and extracted with a hot methanol-water mixture. Collected extracts deposited Cu(*abaDPT*)I_2 which was recrystallized twice from methanol–water mixture to give dark-green crystals.

Physical measurements

IR spectra in the 400–4000 cm^{-1} region were obtained using a Perkin–Elmer Model 621 spectrometer. Spectra of solid samples were recorded as Nujol or hexachlorobutadiene mulls. UV visible, and near IR spectra were obtained with a Beckman DK2 spectrometer using 1 cm stoppered silica cells. EPR spectra were recorded on an X-band spectrometer produced by Polish Academy of Science at room temperature; magnetic field was calibrated with DPPH. PMR spectra were obtained using a Tesla BS 487 80 MHz spectrometer in $CDCl_3$ solution with HMDS as internal reference. Electron impact mass spectra were recorded on a Varian MAT 711 spectrometer at 70 eV.

The magnetic measurements were performed by the Gouy method; Diamagnetic corrections were made employing Pascal's constants.[5] Potentiometric titrations were performed using a Radelkis Model OP-205 precision pH-meter. Conductance measurements were made with a K-58 conducting bridge constructed in the Technical University of Warsaw.

RESULTS AND DISCUSSION

Synthesis of the pentadentate ligand *abaDPT* involves refluxing of 1 equivalent of bis(3-aminopropyl)amine with 2 equivalents of 2-aminobenzaldehyde in benzene solution. The results of elemental analysis (Table 1), PMR spectrum, and

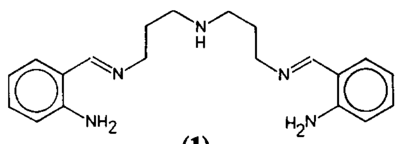
Table 1. Analytical results[a] and molar conductances

	Analysis (%)				λ^c $\left(\frac{cm^2}{\Omega\ mol}\right)$
Compound	C	H	N	X[b]	
abaDPT	71.6 (71.2)	8.08 (8.06)	20.3 (20.7)		
Cu(*abaDPT*)Cl_2	50.7 (50.9)	5.90 (5.77)	14.5 (14.8)	15.1 (15.0)	215
Cu(*abaDPT*)Br_2	42.6 (42.8)	5.00 (4.85)	12.3 (12.5)	28.5 (28.5)	236
Cu(*abaDPT*)I_2	36.7 (36.7)	4.00 (4.16)	10.4 (10.7)	38.5 (38.8)	226
Cu(*abaDPT*)$(NO_3)_2$	45.9 (45.8)	5.00 (5.18)	18.9 (18.7)		217
Cu(*abaDPT*)$(ClO_4)_2$	40.0 (40.0)	4.50 (4.54)	11.4 (11.8)		199
Ni(*abaDPT*)Cl_2	51.4 (51.4)	5.82 (5.82)	15.0 (15.0)	15.1 (15.2)	216
Ni(*abaDPT*)Br_2	43.3 (43.2)	4.88 (4.89)	12.3 (12.6)	28.4 (28.7)	231
Ni(*abaDPT*)I_2	37.2 (37.0)	4.23 (4.18)	10.6 (10.8)	39.4 (39.1)	225
Ni(*abaDPT*)$(NO_3)_2$	46.3 (46.2)	5.30 (5.23)	18.9 (18.9)		212
Ni(*abaDPT*)$(ClO_4)_2$	40.4 (40.4)	4.60 (4.57)	11.9 (11.8)		200

[a] Required values are given in parentheses.

[b] X = Cl, Br, and I.

[c] Molar conductances of 10^{-3} M aqueous solutions at 298 K.



(1)

mass spectrum are consistent with formula (1). A sharp singlet at 8.15 ppm and a broad one at 6.21 ppm in the PMR spectrum are assigned to the azomethine and the NH_2 protons respectively. The bridging methylene protons give rise to three multiplets with baricentres at 3.43, 2.55, and 1.77 ppm respectively. Multiplets of aromatic protons appear in the region of 6.4–7.1 ppm. In the mass spectrum of *abaDPT* a prominent molecular peak is observed at 337 *m/e*, the most abundant fragmentation ions arise from the fissions of C–C bonds within the polyamine chain.

Complexes of empirical formula

M(*abaDPT*)X_2

where M = Cu(II), Ni(II), X = Cl, Br, I, NO_3, and ClO_4 are formed when the ligand dissolved in methanol reacts with metal salts MX_2 dissolved in methanol–water mixture. Elemental analysis (Table 1) and conductance measurements (all complexes are electrolytes in water with molar conductances above 200 Ω^{-1} cm^2 mol^{-1} at concentration of 10^{-3} M, Table 1) suggest that the pentadentate Schiff base coordinates copper and nickel ions as a neutral molecule. All the complexes have reasonably good solubility in water, formamide, and N,N-dimethylformamide, but are insoluble in non-coordinating organic solvents. The solubility characteristics are also consistent with salt formulation.

Infrared spectra have been obtained for ligand and complexes (Table 2). Bands in the 3100–3500 cm^{-1} region, which may be assigned to N–H stretching vibrations of both NH_2 and NH groups, are presented in Fig. 1. It is evident from Fig. 1 and Table

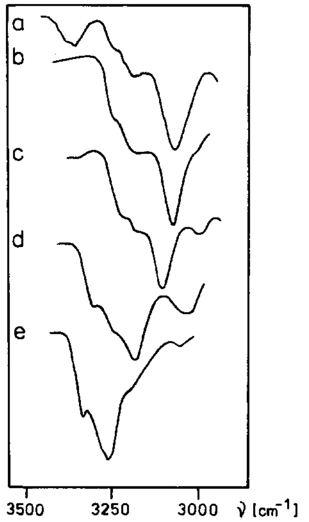


Fig. 1. Part of IR spectra of (a) Cu(*abaDPT*)Cl_2, (b) Cu(*abaDPT*)Br_2, (c) Cu(*abaDPT*)I_2, (d) Cu(*abaDPT*)$(NO_3)_2$, (e) Cu(*abaDPT*)$(ClO_4)_2$ recorded as hexachlorobutadiene mulls.

Table 2. Spectral data for *abaDPT* and complexes

	Infrared[a,b]					Ligand field spectra[a,c]		
Compound	ν_{N-H}			ν_X[d]		ν_{max} (log ε_{max})		
abaDPT	3436m	3272m	3132w					
Cu(*abaDPT*)Cl_2	3370w	3220sh	3172m			16,130 (2.36)	12,120sh	
Cu(*abaDPT*)Br_2	3230sh	3150m				16,130 (2.37)	12,120sh	
Cu(*abaDPT*)I_2	3215sh	3190sh	3100m			16,130 (2.35)	12,120sh	
Cu(*abaDPT*)$(NO_3)_2$	3315w	3260sh	3190m	1742w	1356s	16,130 (2.35)	12,120sh	
Cu(*abaDPT*)$(ClO_4)_2$	3330m	3290sh	3240m	1100s	615m	16,130 (2.35)	12,120sh	
Ni(*abaDPT*)Cl_2	3250sh	3160sh	3140m			18,350 (1.27)	12,200sh	10,530 (0.88)
Ni(*abaDPT*)Br_2	3252m	3190sh	3132m			18,350 (1.30)	12,200sh	10,530 (0.96)
Ni(*abaDPT*)I_2	3230sh	3195m	3130m			18,180 (1.55)	12,200sh	10,530 (0.91)
Ni(*abaDPT*)$(NO_3)_2$	3280m	3246m	3106m	1760w 1365s	1746w	18,350 (1.29)	12,200sh	10,530 (0.89)
Ni(*abaDPT*)$(ClO_4)_2$	3380m	3290m	3230m	1110s	615m	18,350 (1.25)	12,200sh	10,530 (0.99)

[a] Values in cm^{-1}.

[b] Spectra of powdered solids recorded as hexachlorobutadiene mulls.

[c] Measured in aqueous solution.

[d] X = NO_3, ClO_4.

s, strong; m, medium; w, weak; sh, shoulder.

2 data that vibrations of the complexed amino group are influenced by the anions of the outer coordination sphere. A lower frequency of the N–H stretching vibrations in metal halide complexes as compared to metal perchlorate complexes may be due to intramolecular hydrogen bonding between the halide and the NH_2 group, a feature not present in the latter complexes. A similar interaction between the halide and the complexed NH_3 ligand was reported for hexaaminecobalt(III) halides.[6] IR spectra of both copper and nickel perchlorate complexes show a strong band around 1100 cm^{-1} and a medium one at 615 cm^{-1} which indicate a T_d symmetry of ClO_4 and an ionic nature of the complexed metal–ClO_4 bond.[7] Reliable conclusions concerning the bonding of the anion in metal nitrate complexes could not be made from their IR spectra as the main nitrate bands were hidden by the organic ligand bands. However the copper nitrate complex shows a single $\nu_1+\nu_4$ combination band at 1742 cm^{-1} consistent[8] with ionic nitrate group. The spectrum of the nickel nitrate complex exhibits however two weak bands in the 1750 cm^{-1} region separated by 14 cm^{-1}. These bands may accrue from the splitting of $\nu_1+\nu_4$ band, thus indicating the interaction existing between the nitrate and nickel ions[8] in the solid state.

Magnetic moments of solid complexes range from 1.79 to 1.81 B.M. for Cu(*abaDPT*)X_2 and from 2.96 to 2.98 B.M. for Ni(*abaDPT*)X_2 complexes, and show no change with temperature in the 77–298 K range. Magnetic moment data reveal only a small orbital contribution to the predicted spin only value. The evident lack of anomalous moments suggests the absence of appreciable metal–metal interaction in the solid phase.

EPR data of finely powdered Cu(*abaDPT*)X_2 samples are given in Table 3. All the copper complexes show good resolved three g-value spectra (Fig. 2) except of Cu(*abaDPT*)I_2. It had been pointed out earlier[9] that in a three value spectrum with $g_1 < g_2 < g_3$ the value of $R = (g_2-g_1)/(g_3-g_2)$ may indicate the predominant ground state of a mononuclear copper complex containing coordinated nitrogen atoms. Calculated R values (see Table 3) suggest that in Cu(*abaDPT*)Cl_2, Cu(*abaDPT*)$(NO_3)_2$, and Cu(*abaDPT*)$(ClO_4)_2$ a predominant $d_{x^2-y^2}$ ground state is present which may be associated with a structure approximate to square pyramidal geometry. A relatively large value of R for Cu(*abaDPT*)Br_2, much exceeding 1, suggests a predominant d_{z^2} ground state and a structure approximate to trigonal bipyramidal.

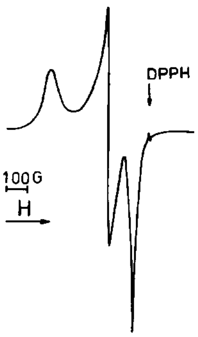


Fig. 2. EPR spectrum of powdered Cu(*abaDPT*)$(ClO_4)_2$.

In order to verify the reliability of the powder g and R values we studied additionally EPR spectra of single crystals of both Cu(*abaDPT*)$(NO_3)_2$ and Cu(*abaDPT*)Br_2.

The former compound crystallizes in the form of rhombic plates while the latter forms small needles. Observation in a polarisation microscope shows that they are not twinned crystals. The angular dependence of the electron spin resonance of Cu(II) measured in single crystal of Cu(*abaDPT*)$(NO_3)_2$ is shown in Fig. 3. It is evident from Fig. 3(b) that the EPR spectrum of a single crystal in a magnetic field oriented perpendicularly to the Z axis [see Fig. 3(a)] consists of two lines which change their separation

Table 3. g-Values for copper complexes[a]

Compound	g_1	g_2	g_3	R[b]	[c]
Cu(*abaDPT*)Cl_2	2.031	2.074	2.202	0.34	$d_{x^2-y^2}$
Cu(*abaDPT*)Br_2	2.028	2.129	2.180	1.81	d_{z^2}
Cu(*abaDPT*)I_2	2.023	[d]	2.171		
Cu(*abaDPT*)$(NO_3)_2$	2.049	2.097	2.182	0.56	$d_{x^2-y^2}$
Cu(*abaDPT*)$(ClO_4)_2$	2.032	2.084	2.207	0.42	$d_{x^2-y^2}$

[a] Measured for powdered samples at room temperature.
[b] Calculated from the relation $R = (g_2-g_1)/(g_3-g_2)$.
[c] Predominant ground state.
[d] Not determined due to a bad resolution.

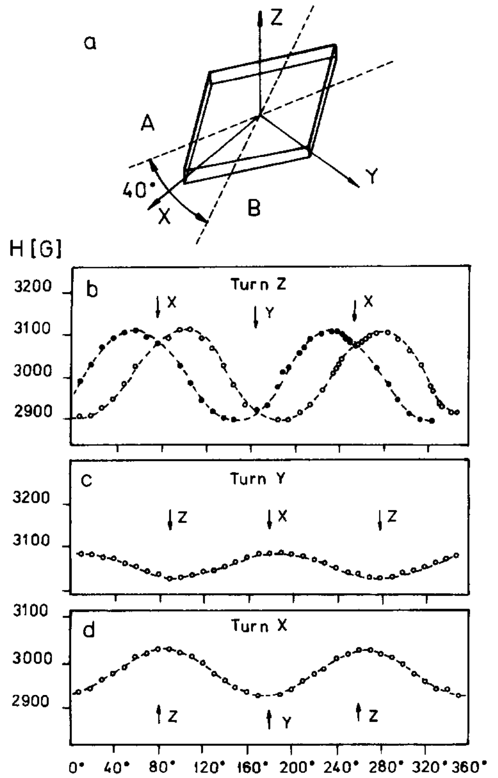


Fig. 3. Angular variation of the EPR of Cu(II) in single crystal of Cu(*abaDPT*)(NO$_3$)$_2$ on rotation around (b) *Z*, (c) *Y*, (d) *X* axis. (a) Schematic representation of the crystal, *X*, *Y*, *Z*: rotation axes, *A*, *B*: principal *g* tensor axes. The magnetic field was always perpendicular to the axis of rotation. Arrows indicate angles at which one of the axes (*X*, *Y*, or *Z*) is parallel to the magnetic field.

during rotation around the *Z* axis. The two lines of equal intensity indicate that copper atoms in crystalline Cu(*abaDPT*)(NO$_3$)$_2$ are incorporated in two magnetically inequivalent places. Based on the described earlier method [10] we constructed the $\langle g^2 \rangle$ matrix from the experimental data, which after diagonalization allowed us to calculate the principal *g* tensor values. They are: $g_{11} = 2.037$, $g_{22} = 2.097$, and $g_{33} = 2.188$. It is interesting to note that the principal *g* tensor axes do not coincide with the *X*, *Y*, and *Z* axes [see Fig. 3(a)]. Two of the principal *g* tensor axes of magnetically inequivalent copper atoms in single crystal of Cu(*abaDPT*)(NO$_3$)$_2$ lie in the *XY* plane [lines *A* and *B* in Fig. 3(a)] forming an angle of approximately 40°. An angular variation study of Cu(*abaDPT*)Br$_2$ reveals the presence of only one copper centre indicating that Cu(II) occupies identical sites in the lattice. Using the aforementioned method we obtained after processing of the data the following principal *g* tensor values for Cu(*abaDPT*)Br$_2$: $g_{11} = 2.032$, $g_{22} = 2.121$, and $g_{33} = 2.168$. Comparing EPR spectra of copper complexes with various Schiff bases comprising a set of five nitrogen donors we see that complexes obtained in this work are of much lower symmetry than those reported by Simmons *et al.*[3] for which axial EPR spectra were observed.

Copper complexes dissolved in water display a broad absorption at 16,130 cm^{-1} ($\varepsilon = 220$) with less defined band around 12,120 cm^{-1}. Hathaway[9] summarized the energy ranges covered by the *d–d* transitions of CuN$_{4-6}$ chromophores of different stereochemistry. The *d–d* bands of Cu(*abaDPT*)X$_2$ complexes fit in well with the range reported for structure of approximate square pyramidal geometry.

Electronic spectra of nickel complexes dissolved in water give bands at 10,530 and 18,350 cm^{-1} which may be interpreted as the spin-allowed transitions $^3T_2$–$^3A_2$ and $^3T_1(F)-{}^3A_2$ respectively in approximately octahedral environment. The weak band which appears as a shoulder at *ca* 12,200 cm^{-1} may result from the distortion of octahedral geometry. We consider the octahedral stereochemistry to arise from the coordination of water molecules to give [Ni(*abaDPT*)H$_2$O]X$_2$ rather than from the coordination of a counter ion leading to [Ni(*abaDPT*)X]X. This observation is in perfect agreement with the results of our electrochemical studies: molar conductances indicate on 2:1 electrolytes and curves obtained as a result of potentiometric titration of nickel halide complexes with silver nitrate were symmetrical with one inflection point at molar ratio of the complex to Ag(I) as 1:2.

Both copper and nickel complexes are very sensitive towards acids. Solutions of Cu(*abaDPT*)X$_2$ even slightly acidified by diluted strong acids change the green colour into a yellow which transforms immediately into a very faint blue. The absorption spectrum of the resultant solution shows a weak *d–d* band at 12,600 cm^{-1} ($\varepsilon = 11$) with a shoulder at 9400 cm^{-1} and resembles closely the spectrum of a hydrated copper(II) ion.[11] In the case of Cu(*abaDPT*)I$_2$ acidification results in the formation of free I$_2$ and CuI. Absorption spectra of nickel complexes in acidic aqueous solution are very similar to the spectrum of the hydrated nickel(II) ion comprising bands at 15,150 ($\varepsilon = 2$), 13,900 ($\varepsilon = 2$), and 8400 cm^{-1} ($\varepsilon = 3$).[12]

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