Journal of Inclusion Phenomena and Macrocyclic Chemistry **35:** 233–242, 1999.

Synthesis, Spectral and Magnetic Characterisation of Copper(II) Dinuclear and Polynuclear Complexes with a Macrocyclic 34-Membered Hexaamine

MAREK PIETRASZKIEWICZ[1,⋆], OKSANA PIETRASZKIEWICZ[1], ROBERT SAF[2], KLAUS HUMMEL[2], ANNA SKORUPA[3] and JERZY MROZIŃSKI[3,∗]
[1]*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44/52, Poland;* [2]*Technischen Universität Graz, A-8010 Graz, Austria;* [3]*Department of Chemistry, University of Wrocław, 14, F. Joliot-Curie , 50-383 Wrocław, Poland*

Abstract. 34-Membered macrocyclic hexaamine containing two independent N_3 donor sets forms homodinuclear copper(II) complexes. Displacements of anions within the copper(II) chloride complexes occurred easily upon addition of different anions to the $CuCl_2$ complex. All new complexes were characterised by elemental analysis, IR, UV/VIS spectroscopy, and magnetic susceptibility measurements. Tetranuclear complexes indicate relation χ_{Cu}^{-1} vs. T in agreement with the Curie–Weiss law. A behaviour anomalous in relation to the phthalate complexes is shown by the $[Cu_4L_2Cl_4(ox)_2]$ complex in which an antiferromagnetic coupling ($J = -53.9$ cm^{-1}) between the Cu^{2+} ions through the $C_2O_4^{2-}$ bridge is observed.

Key words: transition metal complexes, macrocycles, polyamines, magnetism

1. Introduction

Considerable attention has been focused on transition metal complexes with macrocyclic polyamines as mimics of the metalloenzyme active sites [1], redox-active species for electrocatalytic purposes [2], or photoredox molecular devices for converting light energy into other forms [3]. Copper, nickel and cobalt complexes with macrocyclic polyamines have been studied to a great extent, and a number of review articles has been published to date, covering this area [4]. We have been interested in designing and synthesis of redox-active homodinuclear transition metal complexes with macrocyclic polyamines containing two independent N_3 donor sets. We expected that such complexes may bind small molecules to complement their coordination spheres, giving rise to redox processes mimicking active sites in metalloenzymes. We have already demonstrated that availability of macrocyclic hexaamines (as well as octaamines) can be achieved by condensa-

---

[⋆] Author for correspondence.

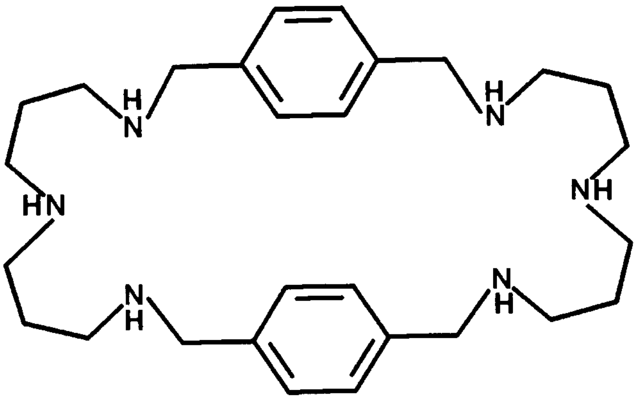

Figure 1. Formula of hexaamine ligand (L).

tion of terephthalic aldehyde with appropriate linear triamines and tetraamines, followed by reduction with lithium aluminum hydride [5] in excellent yield in large quantities. A similar procedure has been published recently by Hay and co-workers [6].

The title ligand L is shown in Figure 1.

Some of the preliminary results involving transition metal complexes with the title ligand have been published [7–10].

Earlier observations that the distances between copper(II) and chloride anions are not equivalent [11], suggested that these two labile chloride ions can be displaced by other anions that bind stronger to copper(II) cations, thus giving rise to polynuclear, mixed anion species of mesoscopic dimensions. Such systems may be of great interest as potential models of redox-active sites in metalloenzymes, or as models of organic zeolites with redox functions. Depending on the nature of the bridging anion between the copper(II) centres it was conceivable to attain a strong magnetic coupling between copper centres that may be of interest in the quest for organic/inorganic hybrid molecular magnetic materials.

2. Experimental

2.1. GENERAL INFORMATION

The hexaamine has been prepared according to the literature [5]. All chemicals have been purchased from Aldrich or Fluka, and used without purification. The IR spectra were obtained on an IR Perkin-Elmer spectrophotometer, and UV/VIS spectra on a Cary 1E (Varian) spectrophotometer. Microanalyses have been done at the Institute of Organic Chemistry of the Polish Academy of Sciences. Titration experiments were performed by addition of calculated amounts of transition metal salts to the macrocyclic hexaamine, and the progress of complex formation was followed by UV/VIS spectroscopy.

Table I. Analytical and spectral data for the copper(II) complexes[#]

Complex No.	Complex formula	Elemental analysis	UV/VIS* λ (nm), ϵ ($cm^{-1}M^{-1}$)	IR (cm^{-1})
1	Cu_2LCl_4	Calcd for: $C_{28}H_{46}Cl_4Cu_2N_6.2CH_3OH$	707 (515)[a]	1020, 1430
		C, 45.06; H, 6.76; N, 10.5	290 (9220)	3440
		Found: C, 45.12; H, 6.92; N, 10.35		
2	$Cu_4L_2Cl_4(Ox)_2$	Calcd for: $C_{60}H_{92}Cl_4Cu_4N_{12}O_8{\cdot}4H_2O$	644 (769)[b]	1620, 1660
		C, 45.68; H, 6.39; N, 10.65	684 (743)	3420
		Found: C, 45.45; H, 6.16, N, 10.39		
3	$Cu_4L_2Cl_4$(phthal)$_2$	Calcd for: $C_{72}H_{100}O_8Cl_4N_{12}Cu_4{\cdot}4H_2O$	634 (670)[b]	1670
		C, 50.23; H, 6.32; N, 9.76	678 (723)	3400
		Found: C, 50.15; H, 6.22; N, 9.67		
4	$Cu_4L_2Cl_4$(isophthal)$_2$	Calcd for: $C_{72}H_{100}O_8Cl_4N_{12}Cu_4{\cdot}4H_2O$	648 (680)[b]	1675
		C, 50.23; H, 6.32; N, 9.76	690 (725)	3450
		Found: C, 50.17; H, 6.25; N, 9.69		
5	$Cu_4L_2Cl_4$(terephthal)$_2$	Calcd for: $C_{72}H_{100}O_8Cl_4N_{12}Cu_4{\cdot}4H_2O$	662 (645)[b]	1660
		C, 50.23; H, 6.32; N, 9.76	685 (710)	3440
		Found: C, 50.15; H, 6.19; N, 9.71		

[#] Abbreviations: ox = oxalate dianion, phthal = phthalate dianion, isophthal = isophthalate dianion, terephthal = terephthalate dianion.

∗ Spectra recorded in: [a] methanol; [b] water.

2.2. COMPLEX FORMATION. GENERAL PROCEDURE

The hexaamine and copper(II) chloride were combined in methanol or acetonitrile in a 1 : 2 ratio and left for crystallisation (complex **1**) [7].

2.3. PREPARATION OF THE Cu(II) OXALATE-CHLORIDE COMPLEX **2**

Complex **1** (0.367 g, 0.5 mmol), dissolved in methanol (10 ml), was treated with potassium oxalate (0.092 g, 0.5 mmol) in 3 ml of water. The blue precipitate which appeared after 2 hours was filtered and crystallised from water. Yield 60%.

2.4. PREPARATION OF THE Cu(II) PHTHALATE/CHLORIDE (**3**), ISOPHTHALATE/CHLORIDE (**4**), AND TEREPHTHALATE/CHLORIDE (**5**) COMPLEXES

These complexes were prepared analogously as above, using the potassium salts of the above-mentioned dicarboxylic acids. The precipitated compounds were filtered after overnight standing. The yields are as follows: **3**: 57%, **4**; 65%, **5**: 53%.

2.5. MAGNETIC MEASUREMENTS

The magnetic susceptibility of polycrystalline samples were measured on a 7221 AC susceptometer/DC magnetometer from Lakeshore Cryotronics Inc. AC measurements were carried out using alternating magnetic fields with a frequency of 125 Hz and a strength of 100 A/m (1.26 Oe), and 1000 A/m (12.6 Oe), respectively. The results were corrected with respect to the signal of the sample holder (gelatine cup). The magnetic susceptibility of complex **4** was collected in the temperature range 1.7–300 K using a Quantum Design SQUID-based magnetometer type MPMS-5. The superconducting magnet was generally operated at field strengths ranging from 1 kG to 50 kG. The SQUID magnetometer was calibrated with a palladium rod sample (Materials Research Corporation, measured purity 99.9985%), for which the gram magnetic susceptibility was taken as 5.30×10^{-6} cm^3 g^{-1} at 293.1 K (National Bureau of Standards, USA).

The corrections for diamagnetism were calculated using Pascal's constants [12] and are shown in Tables II–IV. The effective magnetic moment was calculated from the equation $\mu_{\text{eff}} = 2.83\ (\chi_M \times T)^{1/2}$ (B.M.).

EPR spectra were recorded on a Bruker ER 200 E-SRC spectrometer at temperatures of 293 K and 77 K and for a magnetic field range of 0-5000 G. A frequency meter and nuclear magnetometer were applied for determination of the G parameter.

3. Results and Discussion

3.1. PROPERTIES OF THE COMPLEXES

Hexaamine ligand L formed dinuclear complex **1** with $CuCl_2$ exclusively without formation of the mononuclear complex as we showed in our previous paper on the basis of titration experiments [10]. The spectrophotometric titration was carried out with 3 mL of the ligand L in methanol at the concentration of 10^{-3} M. After each addition of 3 μL of $CuCl_2$ (10^{-1} M in methanol) the absorbance was recorded using a 1 cm quartz cell. The plot of absorbance *versus* metal/ligand ratio indicated the formation of dinuclear complexes in a one-step process (Figure 2).

As indicated from the crystallographic data the distances between copper(II) and chloride anions were not equivalent in **1** [11]. Two of them are longer, so the complexes **2–5** can be formed easily in methanolic, or water solutions by mixing the complex and the dicarboxylates in 1 : 1 ratio. All of them were stable when solids were exposed to the open air. X-ray studies have been conducted on the dioxalate complex **2** [11] and its "sandwich" formula presented in Figure 3 was confirmed.

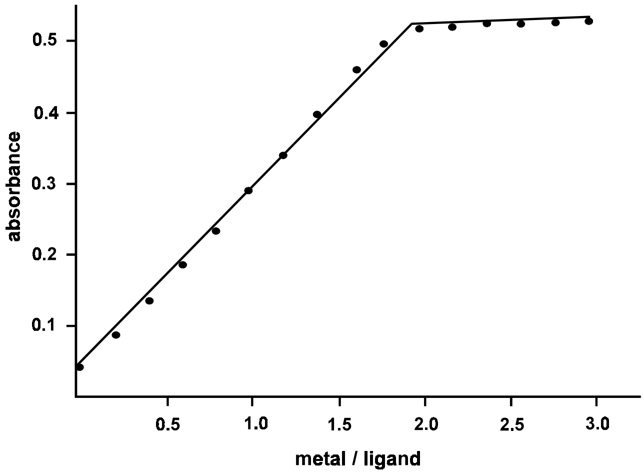

Figure 2. Spectrophotometric titration of L with copper(II) chloride. The plot of absorbance at 707 mm against the metal/ligand ratio.

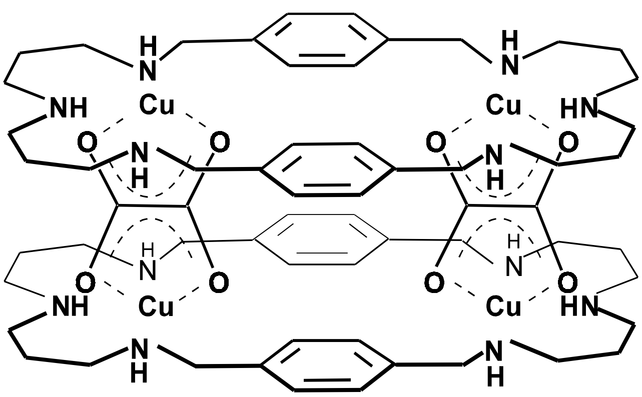

Figure 3. Formula of oxalate complex. Chloride anions are omitted for clarity.

3.2. EPR SPECTRA

Complex **1** gave a characteristic rhombic X-band EPR spectrum for both room temperature and 77 K with $g_1 = 2.04$, $g_2 = 2.12$, $g_3 = 2.21$, $\langle g \rangle = 2.12$ and $g_1 = 2.03$, $g_2 = 2.12$, $g_3 = 2.21$, $\langle g \rangle = 2.12$, respectively. For complex **2** we observed for both temperatures a single line with $g = 2.11$ (room temperature) and $g = 2.12$ (77 K). In contrast, the EPR spectrum of complex **3** is typical for complexes possessing magnetically non-equivalent dimers in their cells for both room temperature and 77 K ($g_1 = 2.05$, $g_2 = 2.16$, $\langle g \rangle = 2.11$ and $g_1 = 2.05$, $g_2 = 2.15$, $\langle g \rangle = 2.10$, respectively). Complex **4** gave an axial EPR spectrum for both temperatures with $g_\parallel = 2.24$, $g_\perp = 2.05$, $\langle g \rangle = 2.13$ (room temperature) and $g_\parallel = 2.24$, $g_\perp = 2.06$, $\langle g \rangle = 2.12$ (77 K). The EPR spectrum of complex **5** at $T = 77$ K gave a single line with g

Table II. Magnetic data of complexes

Complex formula	Mol ($g\ mol^{-1}$)	χ_M* ($cm^3\ mol^{-1}$) in 100 K	μ_{eff}* (B.M.) in 100 K	C ($cm^3\ mol^{-1}$ K) in 4.5–100 K	Θ (K) in 4.5–100 K	$Dia^{corr} \times 10^6$* ($cm^3\ mol^{-1}$)
Cu_2KCl_4	735.6	0.00443	1.86	0.855	−1.73	−172
$Cu_4L_2Cl_4$(phthal)$_2$	1657.6	0.00375	1.69	1.41	−0.61	−183
$Cu_4L_2Cl_4$(isophthal)$_2$	1657.6	0.00492	1.93	1.90	−1.93	−183
Cu_4LCl_4(terephthal)$_2$	1657.6	0.00385	1.76	1.55	−2.04	−183

* The values were calculated per one Cu^{2+} ion.

Table III. Magnetic data of $Cu_4L_2Cl_4$(isophthalate)

T (K)	1.75	2.5	4.0	6.0	8.0	12	15	20
μ_{eff} (B.M.)	1.32	1.44	1.56	1.68	1.79	1.83	1.88	1.90

= 2.10. Increasing the temperature to room temperature caused line splitting which appeared parallel to the component of the line ($g_\perp = 2.09$, $g_\parallel = 2.20$, $\langle g \rangle = 2.13$).

3.3. MAGNETIC DATA AND THEIR INTERPRETATION

The magnetic data for all complexes examined are contained in Tables II–IV.

Of the examined compounds, the Cu_2LCl_4 complex and three complexes with phthalate bridges show paramagnetic properties. At low temperatures, below 20 K, a decrease of the value of magnetic moment is observed, that suggests the occurrence of weak antiferromagnetic interactions. A similarly weak coupling of copper (II) centres has been observed before for copper dimers with phthalate bridges [13–15]. Complex $Cu_4L_2Cl_4$(isophthal)$_2$ showed at low temperatures a strong decrease of the μ_{eff} vs. T value, and it was interesting to check it using the SQUID method (1.7–300 K) (Figure 4).

The results of the measurements gave an agreement with the Curie-Weiss law (χ_{Cu}^{-1} vs. T) and the complex in the whole temperature range is paramagnetic (Table III).

In the case of tetranuclear complexes, the exchange interaction occurs through the phthalate bridges that couple copper ions coming from two different macrocyclic rings, whereas within the dicopper(II) hexaazamacrocyle unit the interactions probably do not occur between two copper(II) centres.

A behaviour anomalous in relation to the others is shown by the Cu(II) complex with an oxalate bridge [$Cu_4L_2Cl_4(ox)_2$] in which an antiferromagnetic coupling between the Cu^{2+} ions through the $C_2O_4^{2-}$ anions is observed (Table IV).

The magnetic susceptibility curve (Figure 5) has a characteristic, wide maximum at the temperature of about $T \approx 80$ K, and at low temperatures ($T \approx 25$ K)

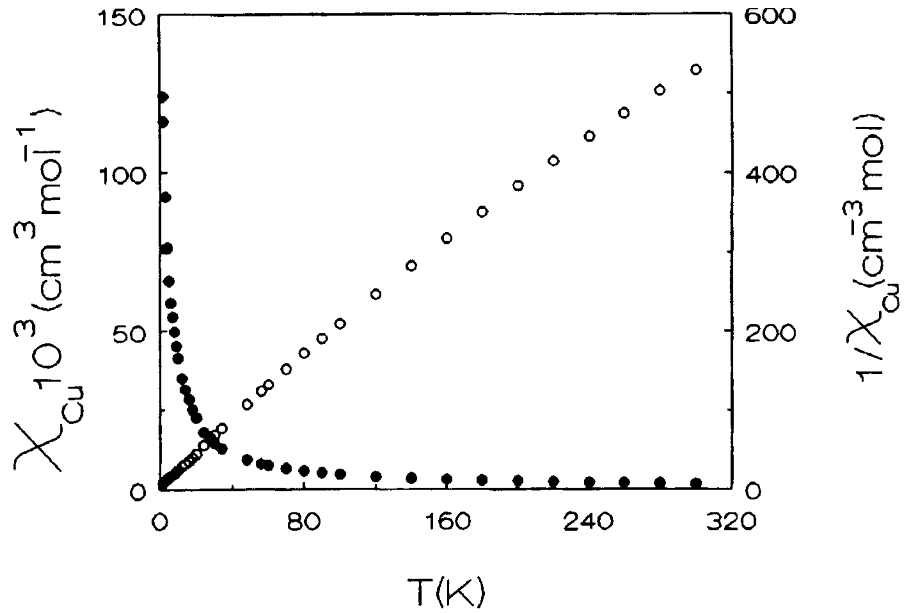

Figure 4. Molar magnetic susceptibility (●) and reciprocal of magnetic susceptibility (○) vs. temperature of $Cu_4L_2Cl_4(ox)_2$ calculated per one Cu^{2+} ion.

Table IV. Magnetic data of $Cu_4Cl_4(ox)_2$

Complex formula	Mol (g mol^{-1})	χ_M* (cm^3 mol^{-1}) in 260 K	μ_{eff}* (B.M.) in 260 K	C (cm^3 mol^{-1} K) in 125–260 K	Θ (K) in 125–260 K	Dia^{corr} × 10^6* (cm^3 mol^{-1})
$Cu_2KCl_4(ox)_2$	1505.4	0.00150	1.77	3.04	−240	−156

* The values were calculated per one Cu^{2+} ion.

a clear minimum occurs, below which the value of the susceptibility rises sharply. This is connected with the occurrence of a monomeric form in the synthesised complex. The interaction between the Cu(II) ions determines the magnitude of the singlet-triplet (2J) split, the value of which has been determined from the temperature dependence of the molar susceptibility, χ_{Cu}, for dimeric complexes, with a monomeric admixture taken into account, using a modified Bleaney–Bowers equation [16].

$$\chi_{Cu} = (Ng^2\beta^2/3\,kT)(1/3 + e^x)(1 - w) + (N\beta^2 g^2/4\,kT)w,$$

where w is the molar fraction of Cu(II) centres engaged in the monomeric form of the complex $x = -2J/kT$

The constants N, β, k and g appearing in this equation have their usual meaning [16]. The values calculated from the above equation are $J = -53.9$ cm^{-1} for $g =$

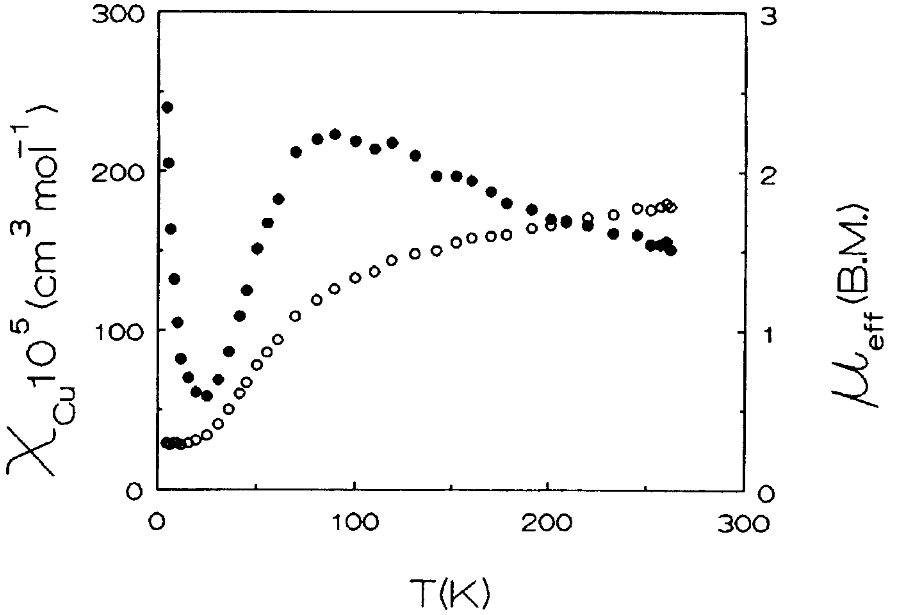

Figure 5. Molar magnetic susceptibility (●) and magnetic moment (○) vs. temperature of $Cu_4L_2Cl_4(ox)_2$ calculated per one Cu^{2+} ion.

2.12 determined from the EPR spectrum, percent of mononuclear impurity = 2.48 and $R = 1.645 \times 10^{-1}$ (R is the agreement factor defined as:

$$R = \sum_{i=1}^{n}[(\chi_{\text{exptl}})_i - (\chi_{\text{theor}})_i]^2 / \sum_{i}(\chi_{\text{exptl}})_i^2).$$

4. Conclusions

Our dinuclear copper(II) complex displayed interesting properties towards selective exchange of two chloride anions for other, strongly binding anions, forming the mixed-anion complexes which may display interesting magnetic properties. It is conceivable that the remaining two chloride anions may be subsequently exchanged for another anions, giving rise to the number of species, either oligomeric, or polymeric. Such coordination polymeric structures are actually of great interest as potential catalysts, photocatalysts, molecular devices, etc. Further directions may involve the use of more complex anions as bridging units, allowing for further interesting magnetic interactions between copper centres. Work in this area is in progress.

Acknowledgement

This work was supported by the State Committee for Scientific Research (Warsaw, Poland).

References

1. M. Shionoya, E. Kimura, and M. Shiro: *J. Am. Chem. Soc*. **115**, 6730 (1993); Y. Murakami, J. Kikuchi, T. Miyajima, and Y. Hisaeda: *Chem. Lett*. 55 (1994); H. Fenniri and J.-M. Lehn: *J. Chem. Soc., Chem. Commun.* 1819 (1993); E. Kimura: *Tetrahedron* **48**, 6175 (1992); T. Oda, R. Irie, T. Katsuki, and H. Okawa: *Synlett.* 641 (1992); M. W. Hosseini and J.-M. Lehn: *J. Chem. Soc., Chem. Commun*. 451 (1991); Y. Murakami, J. Kikuchi, T. Ohno, T. Hirayama, Y. Hisaeda, H. Nishimura, J. P. Snyder, and K. Steliou: *J. Am. Chem. Soc*. **113**, 8229 (1991); J. S. Lindsey, S. Prathapan, T. E. Johnson, and R. W. Wagner: *Tetrahedron* **50**, 8941 (1994); D. P. Riley and R. H. Weiss: *J. Am. Chem. Soc*. **116**, 387 (1994); M. Zheng, S. V. Khangulov, G. C. Dismukes, and V. V. Barynin: *Inorg. Chem*. **33**, 382 (1994); A. M. Reichwein, W. Verboom, and D. N. Reinhoudt: *Recl. Trav. Chim. Pays-Bas* **112**, 595 (1993).
2. P. Horwitz: *Chem. Mater*. **1**, 463 (1989); J.-P. Collin and J.-P. Sauvage: *J. Chem. Soc., Chem. Commun*. 1075 (1987); F. Bedioui, P. Moisy, J. Devynck, L. Salmon, and C. Bied-Charreton: *J. Mol. Catal*. **56**, 267 (1989); F. Lelij, G. Morelli, G. Riccardi, M. Romanelli, A. Rosa, and M. F. Ottaviani: *Polyhedron* **16**, 1911 (1991); C. I. Smith, J. A. Crayston, and R. W. Hay: *J. Chem. Soc., Dalton Trans*. 3267 (1993); E. Fujita, J. Haff, R. Sanzenbacher, and H. Elias: *Inorg. Chem*. **33**, 4627 (1994).
3. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos, and M. Calvin: *J. Chem. Soc., Chem. Commun*. 2105, 1987; V. Balzani: *Tetrahedron* **48**, 10443 (1992); E. Fujita, B. S. Brunschwig, T. Ogata, and S. Yanagida: *Coord. Chem. Rev*. **132**, 195 (1994); C. A. Bignozzi, O. Bortolini, C. Chiorboli, M. T. Indelli, M. A. Rampi, and F. Scandola: *Inorg. Chem*. **31**, 172 (1992); J. Seth, V. Palaniappan, T. E. Johnson, S. Prathapan, J. S. Lindsey, and D. F. Bocian: *J. Am. Chem. Soc*. **116**, 10578 (1994); F. Odobel and J.-P. Sauvage: *New. J. Chem*. **18**, 1139 (1994).
4. A. Bencini, A. Bianchi, and P. Paoletti: *Coord. Chem. Rev*. **120**, 51 (1992); T. A. Kaden: Functionalized tetraazamacrocycles: Ligands with many aspects, in G. W. Gokel (ed.), *Advances in Supramolecular Chemistry*, Vol. 3, JAI Press Inc. (1993), pp. 65–96; D. H. Busch and N. W. Alcock: *Chem. Rev*. **94**, 585 (1994); B. P. Murphy: *Coord. Chem. Rev*. **124**, 63 (1993); R. D. Jones, D. A. Summerville, and F. Basolo: *Chem. Rev*. **39**, 139 (1979); G. McLendon and A. E. Martell: *Coord. Chem. Rev*. **19**, 1 (1976); T. D. Smith and J. R. Pilbrow: *Coord.Chem. Rev*. **39**, 295 (1981); E. C. Niederhoffer, J. H. Timmons, and A. E. Martell: *Chem. Rev*. **84**, 137 (1984); T. A. Kaden: *Topics Curr. Chem*. **121**, 157 (1984).
5. M. Pietraszkiewicz and R. Gąsiorowski: *Chem. Ber*. **123**, 405 (1990).
6. W. Hay, D. T. Richens, G. Wyllie, A. Danby, and T. Clifford: *Trans. Met. Chem*. **387**, 133 (1995).
7. J. McKenzie, H. Toftlund, M. Pietraszkiewicz, Z. Stojek, and K. Słowiński: *Inorg. Chim. Acta* **210**, 143 (1993).
8. K. Słowiński, Z. Kublik, R. Bilewicz, and M. Pietraszkiewicz: *J. Chem. Soc., Chem. Commun*. 1087 (1994).
9. K. Słowiński, R. Bilewicz, Z. Kublik, and O. Pietraszkiewicz: *Polish J. Chem*. **69**, 707 (1995).
10. M. Pietraszkiewicz, O. Pietraszkiewicz, K. Bujno, and R. Bilewicz: *Polish J. Chem.* **72**, 825 (1998).
11. Nguyen-Viet Chinh: Ph.D. Dissertation, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1994).

12. B. König: *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer-Verlag, Berlin (1996).
13. E. G. Bakalbassis, J. Mroziński, and C. A. Tsipis: *Inorg. Chem*. **25**, 3684 (1986).
14. E. G. Bakalbassis, C. A. Tsipis, A. Bozopoulos, W. Dreissing, H. Hartl, and J. Mroziński, *Inorg. Chim. Acta* **186**, 113 (1991).
15. S. Shakhatreh, E. G. Bakalbassis, C. A. Tsipis, and J. Mroziński: *Z. Anorg. Allg. Chem*. **547**, 199 (1989).
16. B. Bleaney and K. D. Bowers: *Proc. R. Soc. London* **A 214**, 451 (1952).