Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 2989-2992

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Spectroscopic Characterization and Theoretical Treatment of Tetradentate Macrocyclic Ligand and Its Transition Metal Complexes

OMAR H. SH. AL-OBAIDI

Chemistry Department, Education College for Women, Al-Anbar University, Ramadi, Iraq

*Corresponding author: E-mail: dromaralobaidi@yahoo.com

(*Received*: 29 June 2011; *Accepted*: 8 February 2012) AJC-11049

Manganese(II), cobalt(II), nickel(II) and copper(II) complexes were synthesized with a novel tetradentate ligand *viz*. 2,9-dithioxo-1,3,8,10-tetraazacyclotetradecane-4,7,11,14-tetraone (L). All the complexes were characterized by analytical and spectral methods such as FT-IR, electronic spectral studies, magnetic susceptibility measurements, atomic absorption, molar conductivity measurements, molar ratio studies and melting points. The molar conductance measurements of the complexes in DMSO correspond to be non-electrolytic nature for all prepared complexes. On the basis of FT-IR and electronic spectral studies all complexes display an octahedral geometry around the metal center, whereas tetragonal for Cu(II) complexes in (1:1) (L:M). A theoretical treatment of the formation of complexes in the gas phase was studied, this was done using the HYPERCHEM-6 program for the molecular mechanics and semi-empirical calculations. The free ligand and its complexes have been tested for their antibacterial activities against two type of human pathogenic bacteria: (*Staphylococcus aureus*), (*Escherichia coli*). The first are Gram positive while the second are Gram negative (by using agar well diffusion method). Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

Key Words: Transition metals, Macrocyclic ligand, Complexes.

INTRODUCTION

The synthesis and characterization of coordination compounds with macrocyclic ligands has evolved as one of the main research areas in coordination chemistry[1-5]. The applications of macrocyclic ligands and their transition metal complexes depends upon the nature of reactants and the corresponding metal ion. The macrocyclic ligands are a growing class of compounds with varying chemistry a wide range of different molecular topologies and set of donor atoms[6-8]. Transition metal macrocyclic complexes have received a great attention because of their biological activities, including antitumor, antibacterial, antiviral, antifungal and anticarcinogenic properties[9-13]. Such biological activities are due to their ability to form tetradentate chelate with essential heavy metal ions, bonding through sulphur, oxygen and nitrogen[14]. The complexes of metal ions in combination to macrocyclic ligands are significant, as these resemble with nature system like porphyrin and cobalamine[15].

In view of the above in this paper we are reporting the synthesis and spectroscopic characterization of macrocyclic Mn(II), Co(II), Ni(II) and Cu(II) complexes with a novel macrocyclic tetradentate nitrogen donor [N_4] ligand (Fig. 1).

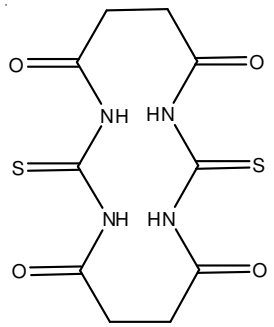

Fig. 1. General structure of ligand

EXPERIMENTAL

All the chemicals used were of AnalaR grade and procured from (BDH Chemicals or Sigma-Aldrich). Metal salts were purchased from Merek and used as received.

Synthesis of ligand (L) (Fig. 1): The hot ethanolic solution (20 mL) of malonic acid (g, 0.05 mol) and a hot ethanolic solution (20 mL) of thiourea (3.80 g, 0.05 mol) were mixed slowly with constant stirring. this mixture was refluxed at -75 ºC for 7 h in the presence of few drops of concentrated hydrochloric acid. Cooling gave an off-white precipitate, which

TABLE-1
SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE PREPARED COMPLEXES

No.	Complexes	Colour	ΔM (Ω^{-1} cm^2mol^{-1}) in DMSO	m.p. (ºC)	Yield (%)	?$_{eff}$ (B M)	UV/VIS λ_{max} (cm^{-1})	Elemental analysis (%) Found (Calcd.)	
								M	Cl
1	$[Mn(L)Cl_2]$	Light brown	18	< 240	71	5.86	17898, 22779, 27136, 36338	12.41 (12.36)	16.06 (16.0)
2	$[Ni(L)Cl_2]$	Orange	17	< 240	65	2.95	10496, 18460, 27982, 36731	13.15 (13.08)	15.91 (15.83)
3	$[Co(L)Cl_2]$	Pink	11	< 240	75	5.02	10373, 14382, 18722, 35696	13.19 (13.13)	15.91 (15.85)
4	$[Cu(L)Cl_2]$	blue	14	235-237	78	1.98	11088, 16598, 27995	14.08 (14.0)	15.74 (15.66)

was filtered, washed with cold EtOH and dried under vacuum. Yield 79 %, m.p. 148-150 ºC. The UV-Vis spectrum in DMSO solvent 240 and 270 nm.

General procedure for preparation of complexes: The hot ethanolic (20 mL) solution of ligand (0.76 g, 0.001 mol) and hot ethanolic (20 mL) solution of corresponding metal salt (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 2-3 h at 55-80 ºC, cooling gives a coloured complexes. it was filtered, washed with cold EtOH and dried under vacuum. The physical properties of prepared complexes are listed in Table-1. The molar ratio of the complexes was determined according to the reported methods[16].

Biological activity for ligand (L) and its metal complexes: The biological activity of the ligand and its metal complexes were studied against two selected type of bacteria which included *Escherichia coli*, as gram negative (-ve) and *Staphylococcus aureus* as gram positive (+ve) to be cultivated and as control for the disc sensitivity test[17]. This method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plat. The plates were incubated for (24 h) at 37 ºC, the zone of inhibition of bacteria growth around the disc was observed.

RESULTS AND DISCUSSION

IR spectrum of the ligand does not exhibit any band corresponding for the free primary diamine and hydroxyl group[18]. Four new bands appear in the spectrum of the free ligand in the regions 1620, 1590, 1248 and 780 cm^{-1} assignable to amide I [ν(C=O)], amide II [ν(C-N) + [δ(N-H)], amide III [δ(N-H)] and amide IV [δ(C=O)] bands, respectively[19,20]. Bands at 795 and 1478 cm^{-1} may be due to the thioamides I and II, respectively. A sharp band observed 3278 cm^{-1}, may be assigned to [ν(N-H)] of the secondary amino group[19].

On the bases of elemental analysis, the complexes were assigned to possess the composition shown in Table-1. The molar conductance measurements of the complexes in DMSO correspond to be non-electrolyte nature for Mn(II), Co(II) Ni(II) and Cu(II). Thus, these complexes may be formulated as $[M(L)Cl_2]$ [where M = Mn(II), Co(II), Ni(II), Cu(II)]. On complex formation the shifting toward lower side of [ν(N-H)] band and the band of amides II and III, suggest the coordination through nitrogen of -NH group $[N_4]$, which is further supported by the appearance of a medium intensity band in the range 485-465 cm^{-1} attributed to ν(M-N).

Manganese(II) complexes: Manganese(II) complexes show magnetic moment at room temperature at 5.86 BM corresponding to five unpaired electrons. Electronic spectra of Mn(II) complexes exhibit four weak beak intensity absorption bands at 17898, 22779, 27136 and 36338 cm^{-1} (Table-1). These bands may be assigned to the transitions: $^1A_{1g} \rightarrow {}^4T_{1g}$ (^4G), $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (^4G) (10B + 5C), $^6A_{1g} \rightarrow {}^4E_g$ (^4D) (17B + C) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4P) (7B + 7C). The parameter B and C were calculated from the second and third transitions because these transitions are free from crystal field splitting and depend on B and C parameters [18,20,21]. The calculated values of the ligand field parameters are given in Table-1.

Cobalt(II) complexes: At room temperature magnetic moment measurements of cobalt(II) complexes at 4.96-5.02 BM corresponding to three unpaired electrons (Table-1). The electronic spectra of all the cobalt(II) complexes display absorption at 10373, 14382, 18722 and 356966 cm^{-1}. These bands may be assigned to the transitions: $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), respectively[21]. It is difficult to give the assignments for the fourth band and it may be due to charge-transfer. The position of electronic spectral bands indicates that these complexes have distorted octahedral geometry[18,20,21].

Nickel(II) complexes: Magnetic moment of the nickel(II) complexes at room temperature 2.95 BM (Table-1). These values are in tune with high spin configuration and show the presence of an octahedral environment[22] around the Ni(II) ion in the complexes. The electronic spectra of the complexes (Table-1) exhibit four bands at 10496, 18460, 27982 and 36731 cm^{-1}. An examination of these bands indicates that the complexes have an octahedral geometry and might possess D_{4h} symmetry[23]. The ground state of Ni(II) in an octahedral coordination is $^3A_{2g}$. Thus, these bands may be assigned to the three spin allowed transitions[21,23], $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively and fourth one may be considered as charge transfer band (Table-1).

Copper(II) complexes: The magnetic moment measurements of the Cu(II) complexes at room temperature lie in the range 1.99 BM (Table-1) corresponding to one unpaired electron[21,24]. Electronic spectra of the copper complexes Table-1 recorded in DMSO possess absorption bands at 11088, 16598 and 27995 cm^{-1}. These bands may be considered to the following three spin allowed[21] transitions: $^2B_{1g} \rightarrow {}^2A_{1g}$ (dx^2-$y^2 \rightarrow dz^2$), $^2B_{1g} \rightarrow {}^2B_{2g}$ (dx^2-$y^2 \rightarrow$dzy), $^2B \rightarrow {}^2E_g$ (dx^2-$y^2 \rightarrow$dxy, dyz), these transitional suggest D_{4h} symmetry. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn-Tellar distortion effect.

Proposed structure: According to the results obtained from (IR, UV/VIS, molar ratio, molar conductivity, atomic absorption) measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown in Fig. (2).

TABLE-2
STRUCTURAL PARAMETERS, BOND LENGTH (Å) AND ANGLES (º) OF THE [Ni(L)Cl_2] COMPLEX

Bond angles (º)		Bond lengths (Å)		Dihedral angles (º)	
N(10)-Ni(22)-N(1)	78.0477	C(13)-H(35)	1.1150	C(9)-N(10)-Ni(22)-Cl(21)	-164.6295
N(10)-Ni(22)-N(3)	130.2139	C(13)-H(34)	1.1169	C(9)-N(10)-Ni(22)-Cl(23)	-81.7126
N(10)-Ni(22)-N(8)	71.8774	C(12)-H(33)	1.1164	C(9)-N(10)-Ni(22)-N(8)	5.3850
N(10)-Ni(22)-Cl(23)	95.3652	C(12)-H(32)	1.1153	C(9)-N(10)-Ni(22)-N(3)	61.1828
N(10)-Ni(22)-Cl(21)	123.0812	N(10)-H(31)	1.0185	C(9)-N(10)-Ni(22)-N(1)	114.6542
N(1)-Ni(22)-N(3)	71.8822	N(8)-H(30)	1.0203	C(11)-N(10)-Ni(22)-Cl(21)	-27.8677
N(1)-Ni(22)-N(8)	104.0294	C(6)-H(29)	1.1169	C(11)-N(10)-Ni(22)-Cl(23)	55.0492
N(1)-Ni(22)-Cl(23)	162.5403	C(6)-H(28)	1.1149	C(11)-N(10)-Ni(22)-N(8)	142.1468
N(1)-Ni(22)-Cl(21)	88.8997	C(5)-H(27)	1.1154	C(11)-N(10)-Ni(22)-N(3)	-162.0554
N(3)-Ni(22)-N(8)	78.0457	C(5)-H(26)	1.1164	C(11)-N(10)-Ni(22)-N(1)	-108.5840
N(3)-Ni(22)-Cl(23)	123.0925	N(3)-H(25)	1.0185	H(31)-N(10)-Ni(22)-Cl(21)	88.6213
N(3)-Ni(22)-Cl(21)	95.3693	N(1)-H(24)	1.0202	H(31)-N(10)-Ni(22)-Cl(23)	171.5381
N(8)-Ni(22)-Cl(23)	88.9212	N(10)-Ni(22)	1.8485	H(31)-N(10)-Ni(22)-N(8)	-101.3642
N(8)-Ni(22)-Cl(21)	162.5635	N(1)-Ni(22)	1.8538	H(31)-N(10)-Ni(22)-N(3)	-45.5664
Cl(23)-Ni(22)-Cl(21)	81.1467	N(3)-Ni(22)	1.8485	H(31)-N(10)-Ni(22)-N(1)	7.9050
O(20)-C(14)-C(13)	122.5491	N(8)-Ni(22)	1.8538	C(2)-N(1)-Ni(22)-Cl(21)	90.6395
O(20)-C(14)-N(1)	122.7201	Cl(23)-Ni(22)	2.1571	C(2)-N(1)-Ni(22)-Cl(23)	145.6018
C(13)-C(14)-N(1)	114.7005	Cl(21)-Ni(22)	2.1571	C(2)-N(1)-Ni(22)-N(8)	-77.5317
O(19)-C(11)-C(12)	123.8117	C(14)-O(20)	1.2100	C(2)-N(1)-Ni(22)-N(3)	-5.3737
O(19)-C(11)-N(10)	123.0379	C(13)-C(14)	1.5290	C(2)-N(1)-Ni(22)-N(10)	-145.1599
C(12)-C(11)-N(10)	112.8805	C(12)-C(13)	1.5473	C(14)-N(1)-Ni(22)-Cl(21)	-41.5196
H(31)-N(10)-Ni(22)	112.5639	C(11)-O(19)	1.2088	C(14)-N(1)-Ni(22)-Cl(23)	13.4427
H(31)-N(10)-C(11)	103.7123	C(11)-C(12)	1.5231	C(14)-N(1)-Ni(22)-N(8)	150.3093
H(31)-N(10)-C(9)	104.5143	N(10)-C(11)	1.3763	C(14)-N(1)-Ni(22)-N(3)	-137.5328
Ni(22)-N(10)-C(11)	112.1238	C(9)-O(18)	1.2054	C(14)-N(1)-Ni(22)-N(10)	82.6810
Ni(22)-N(10)-C(9)	92.2837	C(9)-N(10)	1.3831	H(24)-N(1)-Ni(22)-Cl(21)	-160.4831
C(11)-N(10)-C(9)	131.2488	N(8)-C(9)	1.3881	H(24)-N(1)-Ni(22)-Cl(23)	-105.5209
O(18)-C(9)-N(10)	120.3914	C(7)-O(17)	1.2100	H(24)-N(1)-Ni(22)-N(8)	31.3457
O(18)-C(9)-N(8)	120.7798	C(7)-N(8)	1.3912	H(24)-N(1)-Ni(22)-N(3)	103.5036
N(10)-C(9)-N(8)	103.2834	C(6)-C(7)	1.5290	H(24)-N(1)-Ni(22)-N(10)	-36.2826
H(30)-N(8)-Ni(22)	110.6194	C(5)-C(6)	1.5472	C(2)-N(3)-Ni(22)-Cl(21)	-81.6796
H(30)-N(8)-C(9)	106.9302	C(4)-O(16)	1.2087	C(2)-N(3)-Ni(22)-Cl(23)	-164.5992
H(30)-N(8)-C(7)	104.3776	C(4)-C(5)	1.5232	C(2)-N(3)-Ni(22)-N(8)	114.6628
Ni(22)-N(8)-C(9)	91.8963	N(3)-C(4)	1.3764	C(2)-N(3)-Ni(22)-N(1)	5.3944
Ni(22)-N(8)-C(7)	116.5262	C(2)-O(15)	1.2054	C(2)-N(3)-Ni(22)-N(10)	61.2015
C(9)-N(8)-C(7)	125.8180	C(2)-N(3)	1.3831	C(4)-N(3)-Ni(22)-Cl(21)	55.0634
O(17)-C(7)-N(8)	122.7163	N(1)-C(14)	1.3912	C(4)-N(3)-Ni(22)-Cl(23)	-27.8562
O(17)-C(7)-C(6)	122.5591	N(1)-C(2)	1.3880	C(4)-N(3)-Ni(22)-N(8)	-108.5941
N(8)-C(7)-C(6)	114.6949			C(4)-N(3)-Ni(22)-N(1)	142.1374
				C(4)-N(3)-Ni(22)-N(10)	-162.0555
				H(25)-N(3)-Ni(22)-Cl(21)	171.5636
				H(25)-N(3)-Ni(22)-Cl(23)	88.6440
				H(25)-N(3)-Ni(22)-N(8)	7.9060
				H(25)-N(3)-Ni(22)-N(1)	-101.3624
				H(25)-N(3)-Ni(22)-N(10)	-45.5553
				C(7)-N(8)-Ni(22)-Cl(21)	13.4914
				C(7)-N(8)-Ni(22)-Cl(23)	-41.5027

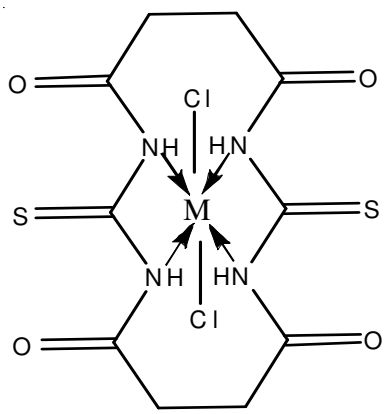

Fig. 2. Proposed structure of complexes where M=Co(II), Ni(II), Cu(II) and Mn(II)

Theoretical study: The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Fig. 3. As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds (Table-2).

Biological activity: The ligand and its transition metal complexes were evaluated against different species of bacteria[25,26]. The antibacterial action of the ligand and the complexes of Mn(II), Ni(II), Co(II) and Cu(II) was checked by the disc diffution technique. This was done on *Staphylococcus aureus* (gram-positive) and *Escherichia coli* (gram-negative) bacteria at 25 ºC. The disc of whatmann no. 4 filter paper having the diameter 6.00 mm were soaked in the solution of compounds

in DMSO (1 mg/mL). After drying it was placed on nutrient agar plates. The inhibition area were observed after 48 h. DMSO used as control (Fig. 4).

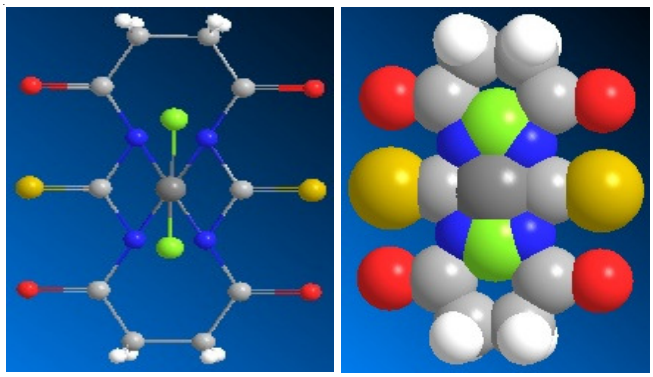

Fig. 3. Optimized structural geometry of Ni(II) complex

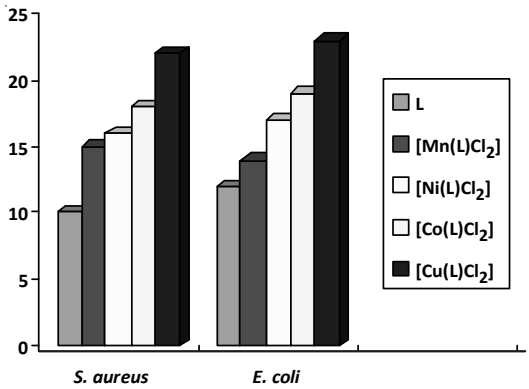

Fig. 4. Effect of ligand and its metal complexes toward bacteria

REFERENCES

1. N.K. Singh, A. Srivastava, A. Sodhi and P. Ranjan, *Transition Met. Chem.*, **25**, 133 (2000).
2. N.P. Singh, V.P. Tyagi and B. Ratnam, *J. Chem. Pharm. Res.*, **2**, 473 (2010).
3. D.P. Singh, K.A. Kumar and R.M. Chopra, *Spectrochim Acta A*, **78**, 629 (2011).
4. A.D. Singh and K. Kumar, *J. Serb. Chem. Soc.*, **75**, 475 (2010); B.D. Singh, V. Grover, K. Kumar and K. Jain, *Acta Chim. Slov.*, **57**, 775 (2010).
5. M.P.L. Alberca, M.J. Mancheno, I. Fernandez, M.G. Gallego, M.A. Sierra, C. Hammert and H. Gornitzka, *Eur. J. Inorg. Chem.*, **6**, 842 (2011).
6. K.Y. Choi, H.Y. Lee, B. Park, J.H. Kim, J. Kim, M.W. Ryu, M. Suh and H. Suh, *Polyhedron*, **20**, 2003 (2001).
7. T.W. Hambley, L.F. Lindoy, J.R. Reimers, P. Turner, W. Wei and A.N.W. Cooper, *J. Chem. Soc., Dalton Trans*, 614 (2001).
8. E.Q. Gao, H.Y. Sun, D.Z. Liao, Z.H. Jiang and S.P. Yan, *Polyhedron*, **21**, 359 (2002).
9. A.P. Mishra, R.K. Mishra and S.P. Shrivastava, *J. Serb. Chem. Soc.*, **74**, 523 (2009).
10. G. Pemawat, R.R. Dangi and G.L. Talesara, *J. Indian Chem. Soc.*, **87**, 1351 (2010).
11. M. Canedas, E.L. Torres, A.M. Aris, M.A. Mendrila and M.T. Sevilla, *Polyhedron*, **19**, 2059 (2000).
12. E. Labisbal, A. Sousa, A. Castineiras, A. Graciavazques, J. Romero and D.X. West, *Polyhedron*, **19**, 1255 (2000).
13. O.D. Fox, M.G.B. Drew, E.J.S. Wilkinson and P.O. Beer, *Chem. Commun.*, 319 (2000).
14. S. Chandra, D. Jain and B. Ratnam, *J. Indian. Chem. Soc.*, **87**, 1379 (2010).
15. R.F. Keys, J.J. Carter, E.E. Englud, M.M. Daly, G. Nilius and Z. Ma, *J. Med. Chem.*, **46**, 1795 (2003).
16. H.H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
17. Z.H. Chohan and M. Praveen, *Metal-Based Drugs*, **6**, 95 (1999).
18. S. Chandra and K. Gupta, *Transition Met. Chem.*, **27**, 329 (2002).
19. S. Chandra and L.K. Gupta, *J. Saudi Chem. Soc.*, **7**, 243 (2003); C.R.K. Rao and P.S. Zacharias, *Polyhedron*, **16**, 1201 (1977).
20. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York (1970).
21. A.B.P. Lever, Crystal Field Spectra. Inorganic Electronic Spectroscopy, 1st. ed., Elsevier, Amsterdam (1968).
22. A. Bansal and R.V. Singh, *Indian J. Chem.*, **40A**, 989 (2001).
23. W.G. Hanna and M.M. Moawad, *Transtion Met. Chem.*, **26**, 644 (2001).
24. S. Chandra and L.K. Gupta, *Transition Met. Chem.*, **77**, 196 (2002).
25. M.A. Pujar, B.S. Hadimani, S. Meenakumari, S.M. Gadded and Y.F. Neelgund, *Curr. Sci.*, **55**, 353 (1986).
26. S. Chandra and S.D. Sharma, *J. Indian Chem. Soc.*, **79**, 495 (2002).