Neutral Cu_4N_{12} and Ag_4N_{12} metallacycles with a *para*-cyclophane framework assembled from copper(I) and silver(I) pyrazolates and pyridazine†

H. V. Rasika Dias,* Himashinie V. K. Diyabalanage and Chammi S. Palehepitiya Gamage

Received (in Columbia, MO, USA) 3rd December 2004, Accepted 10th January 2005
First published as an Advance Article on the web 28th January 2005
DOI: 10.1039/b418306a

Trinuclear copper(I) and silver(I) pyrazolates {[3,5-$(CF_3)_2$Pz]M}$_3$ (M = Cu and Ag) react with pyridazine to give neutral, tetranuclear metallacycles with a *para*-cyclophane core whereas benzo[*c*]cinnoline fails to break the cyclic pyrazolate trimers under similar conditions, and affords a metallapropellane featuring both two- and three-coordinate metal sites.

Synthesis of geometrically shaped metallacycles through metal–ligand complexation methodology is an area of significant current interest.[1–7] Products of these reactions show promise in various applications like selective sensors, sorters, gas storage, catalysis, and luminescent materials. Nitrogen ligands based on pyridine, pyridazine. pyrimidine, and pyrazine are commonly used as scaffolds in the synthesis of such metallacycles. Although a large number of coordination complexes with diverse two- and three-dimensional architectures are known, the vast majority of these are ionic species. We are interested in the synthesis and properties of neutral coordination networks since they do not have free counter ions to complicate the assembled structures and to occupy part of the empty space.[8,9] This article describes the assembly of neutral metal–nitrogen based metallacycles with a cyclophane framework[5,10–12] using copper(I) and silver(I) pyrazolates and pyridazine. The isolation of a Y-shaped metallacycle that could be viewed as a model for a possible intermediate during the metalla-aza-cyclophane formation process is also described.

Treatment of copper(I) pyrazolate {[3,5-$(CF_3)_2$Pz]Cu}$_3$ (**1**)[13] with the bidentate nitrogen ligand pyridazine ($C_4H_4N_2$) in 1:1.5 molar ratio led to a golden yellow crystalline product [{3,5-$(CF_3)_2$Pz}$_4$Cu$_4$($C_4H_4N_2$)$_2$] (**2**) in 90% yield. The X-ray structure shows that it features a *para*-cyclophane core composed of four copper and twelve nitrogen atoms (Fig. 1). This tetranuclear copper complex [{3,5-$(CF_3)_2$Pz}$_4$Cu$_4$($C_4H_4N_2$)$_2$] sits about a crystallographic inversion center. Each copper atom is bonded to three nitrogens in a trigonal planar geometry. The Cu1–Cu2 (or Cu1A–Cu2A) separation of 2.940 Å is only slightly longer than two times 1.40 Å, which is the van der Waals radius of copper. The Cu1–Cu2A separation is much longer (3.302 Å). The dinuclear copper pyrazolate moiety, Cu(μ-N-N)$_2$Cu adopts a boat conformation. The related compound {[3,5-$(CF_3)_2$Pz]Cu(2,4,6-collidine)}$_2$ (**3**),[14] which has been obtained from a reaction of {[3,5-$(CF_3)_2$Pz]Cu}$_3$ with the monodentate ligand 2,4,6-collidine, also has a Cu(μ-N-N)$_2$Cu unit. However, its Cu(μ-N-N)$_2$Cu core is planar with a Cu–Cu separation of 3.394 Å. There are a few compounds in the literature that feature Cu_4N_{12} metallacycles, like [Cu$_4$(atdz)$_6$](ClO$_4$)$_4$ (where, atdz = 2-amino-1,3,4-thiadiazole),[15]

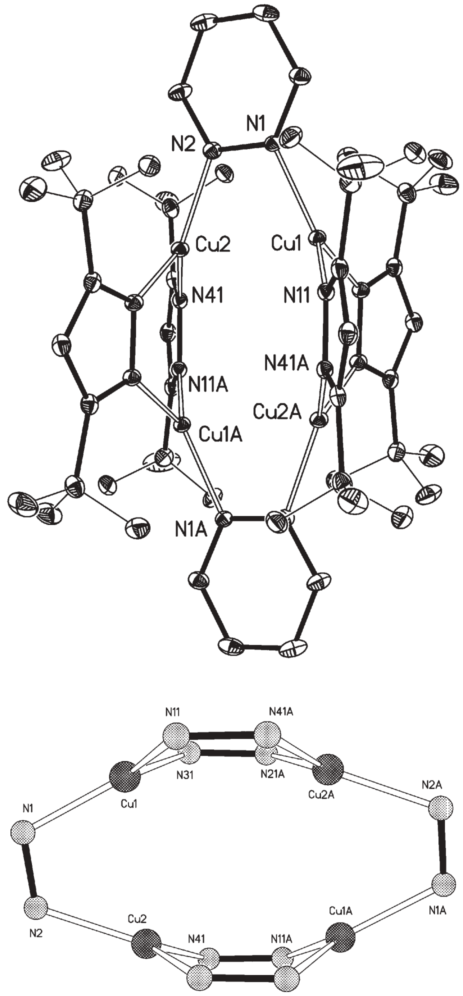
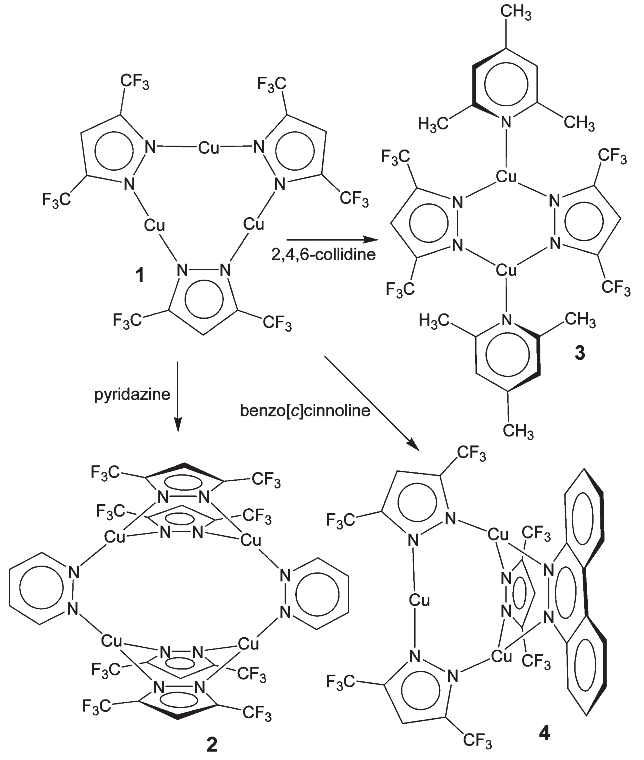


Fig. 1 Top, molecular structure of [{3,5-$(CF_3)_2$Pz}$_4$Cu$_4$($C_4H_4N_2$)$_2$], hydrogen atoms have been removed for clarity; bottom, Cu_4N_{12} metallacycle. Selected bond lengths (Å) and angles (°): Cu(1)–N(11) 1.945(2), Cu(1)–N(1) 1.951(2), Cu(1)–N(31) 1.976(2), Cu(1)···Cu(2) 2.9398(5), Cu(2)–N(41) 1.962(2), Cu(2)–N(2) 1.963(2), Cu(2)–N(21) 1.987(2); N(11)–Cu(1)–N(1) 130.08(8), N(11)–Cu(1)–N(31) 113.06(8), N(1)–Cu(1)–N(31) 116.85(8), N(41)–Cu(2)–N(2) 128.53(8), N(41)–Cu(2)–N(21) 114.24(8), N(2)–Cu(2)–N(21) 117.11(8).

---

† Electronic supplementary information (ESI) available: full experimental details for [{3,5-$(CF_3)_2$Pz}$_4$M$_4$($C_4H_4N_2$)$_2$] (M = Cu, Ag) and [{3,5-$(CF_3)_2$PzCu}$_3$($C_{12}H_8N_2$)]; crystallographic data (.cif files) have been deposited with CCDC. See http://www.rsc.org/suppdata/cc/b4/b418306a/
*dias@uta.edu

$[Cu_4(C_4H_4N_2)_6](ClO_4)_4$[16] and $(Et_3NH)_2[\{3,5\text{-}(CH_3)_2,4\text{-}(NO_2)Pz\}_6Cu_4]$.[17] They are however, ionic compounds.



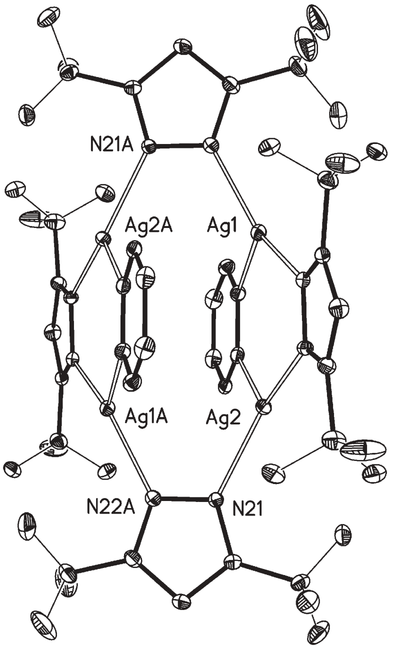


Fig. 2 Molecular structure of $[\{3,5\text{-}(CF_3)_2Pz\}_4Ag_4(C_4H_4N_2)_2]$, hydrogen and fluorine atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–N(11) 2.165(3), Ag(1)–N(22) 2.212(3), Ag(1)–N(2) 2.381(3), Ag(2)–N(12) 2.170(3), Ag(2)–N(21) 2.213(3), Ag(2)–N(1) 2.393(3)°; N(11)–Ag(1)–N(22) 143.36(11), N(11)–Ag(1)–N(2) 118.55(11), N(22)–Ag(1)–N(2) 97.35(11), N(12)–Ag(2)–N(21) 139.97(11), N(12)–Ag(2)–N(1) 117.97(11), N(21)–Ag(2)–N(1) 100.15(11).

Interestingly, the silver(I) pyrazolate $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$[13] also reacts with pyridazine to give $[\{3,5\text{-}(CF_3)_2Pz\}_4Ag_4(C_4H_4N_2)_2]$ with a *para*-cyclophane framework. It is a colorless solid, and crystallizes with a center of inversion in the $P2_1/c$ space group. There are two chemically similar but crystallographically different molecular halves in the asymmetric unit. The *para*-cyclophane core consists of four silver and twelve nitrogen atoms (Fig. 2). However, in contrast to the copper analog, the pyrazolyl moieties (rather than the pyridazines) act as bridges that link the two six membered $Ag(\mu\text{-}N\text{-}N)_2Ag$ fragments. The ionic compound $[Ag_4(atdz)_6](ClO_4)_4$ has somewhat similar five membered ring bridges.[15] The angle between the least squares plane of the $Ag(\mu\text{-}N\text{-}N)_2Ag$ unit and the Ag_4 plane is about 50°, indicating significant deviation (of about 40°) from the orthogonal orientation. The copper analog shows much smaller deviation from the orthogonality (about 17°). The silver centers of $[\{3,5\text{-}(CF_3)_2Pz\}_4Ag_4(C_4H_4N_2)_2]$ are three coordinate and adopt trigonal planar geometry. The closest Ag–Ag separation of 3.477 Å is only slightly longer than the sum of the van der Waals radii of two silver atoms (3.44 Å). Although there are two different types of pyrazolyl environments in $[\{3,5\text{-}(CF_3)_2Pz\}_4Ag_4(C_4H_4N_2)_2]$, the solution NMR data indicate only one set of signals. This may be a result of a fluxional process that makes the pyrazolyl groups equivalent on the NMR timescale or having accidental isochronous chemical shifts.

Encouraged by this simple, facile tetranuclear metallacycle assembly process, we decided to investigate the coordination chemistry of other diazine ligands like benzo[*c*]cinnoline with metal pyrazolates. Although benzo[*c*]cinnoline is structurally similar to pyridazine, the reaction with copper(I) pyrazolate $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ under similar conditions did not lead to the break-up of the Cu_3N_6 metallacycle and the formation of a molecule with a cyclophane framework. This is perhaps due to the relatively low basicity of benzo[*c*]cinnoline.[18] Nevertheless it afforded an interesting Y-shaped molecule, $[\{3,5\text{-}(CF_3)_2PzCu\}_3(C_{12}H_8N_2)]$ (**4**), featuring a highly distorted nine-membered Cu_3N_6 metallacycle. This compound was obtained in 95% yield by reacting $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and benzo[*c*]cinnoline at the optimum molar ratio of 1:1.

X-ray crystallographic data of $[\{3,5\text{-}(CF_3)_2PzCu\}_3(C_{12}H_8N_2)]$ show that the benzo[*c*]cinnoline coordinates to two of the three copper atoms of $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ (Fig. 3). The Cu3 atom adopts a linear geometry (as observed in the precursor) whereas Cu1 and Cu2 centers have trigonal planar geometry. The closest Cu···Cu separation is between Cu1 and Cu2 (3.031 Å). The overall molecule may be viewed as an intermediate between $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ with a planar structure and $[\{3,5\text{-}(CF_3)_2Pz\}_4Cu_4(C_4H_4N_2)_2]$ with the cyclophane skeleton. ^1H, and ^{19}F NMR data of $[\{3,5\text{-}(CF_3)_2PzCu\}_3(C_{12}H_8N_2)]$ in $CDCl_3$ at the room temperature show sharp signals indicating the presence of just one pyrazolyl ring environment on the NMR timescale, indicating a possible fluxional process. It is also possible to synthesize the silver analog $[\{3,5\text{-}(CF_3)_2PzAg\}_3(C_{12}H_8N_2)]$ using $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ and benzo[*c*]cinnoline.[19]

In summary, we have described a simple route to obtain *neutral* metallacycles with Cu_4N_{12} and Ag_4N_{12} *para*-cyclophane skeletons. It is also possible to isolate the products with the partially assembled cyclophane framework. These compounds are fairly stable in air, and soluble in a variety of common organic solvents including hexane. In addition to the structural interest, compounds

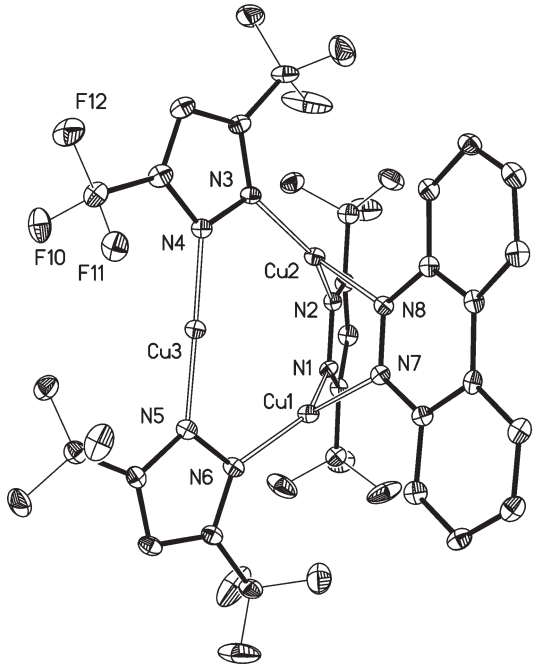


Fig. 3 Molecular structure of [{3,5-$(CF_3)_2$PzCu}$_3$($C_{12}H_8N_2$)], hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(6) 1.930(4), Cu(1)–N(1) 1.936(4), Cu(1)–N(7) 2.125(4), Cu(2)–N(2) 1.929(4), Cu(2)–N(3) 1.943(4), Cu(2)–N(8) 2.130(4), Cu(3)–N(5) 1.864(4), Cu(3)–N(4) 1.866(4), Cu(1)···Cu(2) 3.0311(10); N(6)–Cu(1)–N(1) 140.84(18), N(6)–Cu(1)–N(7) 109.28(17), N(1)–Cu(1)–N(7) 108.04(17), N(6)–Cu(1)–Cu(2) 122.23(13), N(1)–Cu(1)–Cu(2) 64.03(12), N(7)–Cu(1)–Cu(2) 66.88(12), N(2)–Cu(2)–N(3) 146.80(18), N(2)–Cu(2)–N(8) 105.45(17), N(3)–Cu(2)–N(8) 106.55(17), N(2)–Cu(2)–Cu(1) 64.41(13), N(3)–Cu(2)–Cu(1) 123.49(13), N(8)–Cu(2)–Cu(1) 64.81(11), N(5)–Cu(3)–N(4) 178.8(2).

like [{3,5-$(CF_3)_2$Pz}$_4$$Cu_4$($C_4H_4N_2$)$_2$] and [{3,5-$(CF_3)_2$PzCu}$_3$($C_{12}H_8N_2$)] may also have interesting photophysical properties. {[3,5-$(CF_3)_2$Pz]Cu}$_3$ for example, is a brightly luminescent compound.[20] Furthermore, the emitted colors depend on the solvent, temperature, and concentration. The copper and silver collidine adducts {[3,5-$(CF_3)_2$Pz]M(2,4,6-collidine)}$_2$ are blue emitters.[14]

We are currently investigating the chemistry of coinage metal pyrazolates with other nitrogen ligands, as well as luminescent properties of [{3,5-$(CF_3)_2$Pz}$_4$$M_4$($C_4H_4N_2$)$_2$] and [{3,5-$(CF_3)_2$PzM}$_3$($C_{12}H_8N_2$)].‡

We thank the Robert A. Welch Foundation (grant Y-1289) and the National Science Foundation (CHE-0314666) for financial support of this research, and Doug Powell (University of Kansas) for collecting X-ray data of two compounds.

H. V. Rasika Dias,* Himashinie V. K. Diyabalanage and
Chammi S. Palehepitiya Gamage
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas, 76019-0065, USA. E-mail: dias@uta.edu

Notes and references

‡ **[{3,5-$(CF_3)_2$Pz}$_4$$Cu_4$($C_4H_4N_2$)$_2$]**: Yield 90%. X-ray quality crystals were grown from hexane at 6 °C. Mp: 127–128 °C; ^{1}H NMR ($CDCl_3$): δ 9.10 (br s, $H_{3',6'}$, 4H); 7.65 (br s, $H_{4',5'}$, 4H); δ 6.87 (s, Pz-H, 4H); ^{19}F NMR ($CDCl_3$): δ −60.4 (s, CF_3); crystal data for [{3,5-$(CF_3)_2$Pz}$_4$$Cu_4$($C_4H_4N_2$)$_2$]. $C_{28}H_{12}Cu_4F_{24}N_{12}$, $M = 613.33$, $T = 100(2)$ K, Triclinic, $a = 9.3177(10)$ Å, $b = 10.0414(11)$ Å, $c = 11.7532(13)$ Å, $\alpha = 105.928(2)°$, $\beta = 109.526(2)°$, $\gamma = 96.780(2)°$, $V = 969.56(18)$ Å^3, space group $P\bar{1}$, $Z = 1$, $\mu = 2.323$ mm^{-1}, 6176 reflections collected, 3685 unique [$R_{int} = 0.0159$], The final R (all data), $R_1 = 0.0312$, $wR_2 = 0.0824$.

[{3,5-$(CF_3)_2$Pz}$_4$$Ag_4$($C_4H_4N_2$)$_2$]: Yield 95%. X-ray quality crystals were grown from hexane at 6 °C. Mp: 124–125 °C; ^{1}H NMR ($CDCl_3$): δ 9.02 (t, $^3J_{HH} = 3.6$ Hz, $H_{3',6'}$, 4H); 7.52 (t, $^3J_{HH} = 3.6$ Hz, $H_{4',5'}$, 4H); δ 6.95 (s, Pz-H, 4H); ^{19}F NMR ($CDCl_3$): δ −60.9 (s, CF_3); crystal data for [{3,5-$(CF_3)_2$Pz}$_4$$Ag_4$($C_4H_4N_2$)$_2$]. $C_{28}H_{12}Ag_4F_{24}N_{12}$, $M = 1403.98$, $T = 101(2)$ K, Monoclinic, $a = 18.142(2)$ Å, $b = 22.807(3)$ Å, $c = 10.0462(12)$ Å, $\beta = 104.477(2)°$, $V = 4024.7(8)$ Å^3, space group $P2_1/c$, $Z = 4$, $\mu = 2.071$ mm^{-1}, 22956 reflections collected, 6991 unique [$R_{int} = 0.0245$], The final R (all data), $R_1 = 0.0329$, $wR_2 = 0.0788$.

[{3,5-$(CF_3)_2$PzCu}$_3$($C_{12}H_8N_2$)]: Yield 95%. X-ray quality red crystals were grown from CH_2Cl_2 at −25° C. Mp: 219–222 ° C, ^{1}H NMR ($CDCl_3$): δ 6.94 (s, Pz-H, 3H), 7.88 (apparent td, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 1.3$ Hz, $H_{5',8'}$, 2H), 7.95 (apparent td, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.0$ Hz, $H_{4',9'}$, 2H), 8.53 (d, $^3J_{HH} = 8.5$ Hz, $H_{6',7'}$, 2H), 8.58 (d, $^3J_{HH} = 8.0$ Hz, $H_{3',10'}$, 2H); ^{19}F NMR($CDCl_3$): δ −60.6 (s, CF_3); crystal data for [{3,5-$(CF_3)_2$PzCu}$_3$($C_{12}H_8N_2$)]·CH_2Cl_2. $C_{28}H_{13}Cl_2Cu_3F_{18}N_8$, $M = 1064.98$, $T = 100(2)$ K, Monoclinic, $a = 9.2674(14)$ Å, $b = 15.769(2)$ Å, $c = 23.946(4)$ Å, $\beta = 99.060(2)°$, $V = 3455.7(9)$ Å^3, space group $P2_1/n$, $Z = 4$, $\mu = 2.119$ mm^{-1}, 27148 reflections collected, 6798 unique [$R_{int} = 0.0442$], The final R (all data), $R_1 = 0.0665$, $wR_2 = 0.1444$.

Crystallographic data (.cif files) for the structures reported here have been deposited with the Cambridge Crystallographic Data Center: CCDC 257594–257596. See http://www.rsc.org/suppdata/cc/b4/b418306a/ for crystallographic data in .cif or other electronic format.

1 G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
2 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.
3 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.
4 S.-S. Sun and A. J. Lees, *Coord. Chem. Rev.*, 2002, **230**, 171.
5 C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289.
6 F. Wuerthner, C.-C. You and C. R. Saha-Moeller, *Chem. Soc. Rev.*, 2004, **33**, 133.
7 M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.
8 F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 575.
9 M. L. Kuhlman and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2003, **125**, 10084.
10 R. Lin, J. H. K. Yip, K. Zhang, L. L. Koh, K.-Y. Wong and K. P. Ho, *J. Am. Chem. Soc.*, 2004, **126**, 15852, and the references therein.
11 X. Ottenwaelder, J. Cano, Y. Journaux, E. Riviere, C. Brennan, M. Nierlich and R. Ruiz-Garcia, *Angew. Chem., Int. Ed.*, 2004, **43**, 850.
12 P. J. Cragg, F. R. Heirtzler, M. J. Howard, I. Prokes and T. Weyhermueller, *Chem. Commun.*, 2004, 280.
13 H. V. R. Dias, S. A. Polach and Z. Wang, *J. Fluorine Chem.*, 2000, **103**, 163.
14 M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage and H. V. R. Dias, *Inorg. Chem.*, 2003, **42**, 8612.
15 M. Maekawa, M. Munakata, T. Kuroda-Sowa, Y. Suenaga and K. Sugimoto, *Inorg. Chim. Acta*, 1999, **290**, 153.
16 M. Maekawa, M. Munakata, T. Kuroda-Sowa and Y. Nozaka, *J. Chem. Soc., Dalton Trans.*, 1994, 603.
17 G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, A. Maspero and M. Moret, *Inorg. Chem.*, 1998, **37**, 4284.
18 H. J. S. Machado and A. Hinchliffe, *Theochem*, 1995, **339**, 255.
19 H. V. R. Dias and C. S. Palehepitiya Gamage, unpublished results.
20 H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman and M. A. Omary, *J. Am. Chem. Soc.*, 2003, **125**, 12072.