Crystal Structure of an Antiferromagnetically Coupled μ-Carbonato-bridged Dinickel(II) Complex Containing the Pendent-arm Macrocycle 1-(3-Dimethylaminopropyl)-1,5,9-triazacyclododecane (L¹); a System which readily sequesters Carbon Dioxide from Air

Simon C. Rawle,[a] Charlie J. Harding,[b] Peter Moore*[a] and Nathaniel W. Alcock[a]

[a] Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK
[b] Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

The nickel(II) complex of the pendent-arm macrocycle 1-(3-dimethylaminopropyl)-1,5,9-triazacyclododecane (L¹) sequesters CO_2 from air to yield, after addition of thiocyanate ion, $[\{(HL^1)Ni(NCS)\}_2(CO_3)]^{2+}$, the first example of a μ-carbonato dinickel(II) complex; the Ni atoms are antiferromagnetically coupled with the exceptionally large exchange constant $-2J = 94.6 \pm 0.4$ cm^{-1}.

As part of a programme to design ligands to enforce tetrahedral coordination of first-row transition metal ions, we reported previously that the propyl-linked pendent-arm macrocycle 1-(3-dimethylaminopropyl)-1,5,9-triazacyclodo-decane (L¹) forms a tetrahedral complex with Zn^{II}.[1] In Ni^{II} and Cu^{II} complexes, however, the electronic demands of the metal override the stereochemical preferences of this and related ligands, so that anions or solvent molecules enter the coordination sphere to yield five- and six-coordinate structures.[2]

In an attempt to isolate a five-coordinate Ni^{II} complex of L¹, the ligand (128 mg, 0.5 mmol) was added to $[Ni(MeCN)_6]$-$(ClO_4)_2$ (252 mg, 0.5 mmol)[3] in acetonitrile (5 cm³) containing one equivalent (40 mg, 0.5 mmol) of sodium thiocyanate. The resulting mauve solution was treated with an excess of concentrated aqueous sodium perchlorate. After filtration and standing in air for four days, the six-coordinate complex $[\{(HL^1)Ni(NCS)\}_2(CO_3)](ClO_4)_2\cdot3H_2O$ crystallised from the solution in 60% yield as hexagonal blue plates. [In MeCN, λ_{max}/nm (ε/dm³ mol^{-1} cm^{-1}): 374 (92); 598 (53); 1028 (21).] Identical yields of product were obtained on evaporation in an atmosphere of CO_2, or on addition of $NaHCO_3$ (0.5 equiv.) to the solution followed by evaporation under nitrogen. The complex rapidly liberates CO_2 on treatment with dilute acid.

Tanase et al. recently reported that $[Ni(Me_2en)_3]^{2+}$ (Me_2en = N,N-dimethylethane-1,2-diamine) also efficiently fixes atmospheric carbon dioxide.[4] The proposed mechanism involves initial loss of one Me_2en ligand molecule from the tris complex, the liberated diamine then assisting the hydration of

CO_2 to produce CO_3^{2-} which is taken up by the bis complex $[Ni(Me_2en)_2]^{2+}$. CO_2 fixation in the present case probably follows a similar pathway, utilising a dimethylamino group on an uncoordinated pendent arm. The Zn^{II} complex of L¹ is known to be unstable, mainly owing to the presence of the sterically hindered tertiary amine donor.[1,2] Such steric effects increase in octahedral complexes of nickel(II), and in aqueous solution the pendent arm of L¹ doubtless fails to coordinate the central ion. Thus, the dimethylamino group is available in solution to set up a base-assisted hydration of atmospheric carbon dioxide. As observed by Tanase and Yano,[4] the presence of a dimethylamino group in the ligand seems critical for efficient CO_2 uptake; neither L² nor 12N3 give μ-carbonato complexes as readily under similar conditions. However, 12N3 forms $[\{(12N3)Ni(OH_2)_2CO_3][ClO_4]_2$ (based on the FAB mass spectrum and a C, H, N analysis) in the presence of an excess of 12N3, showing that neither the thiocyanate ions nor the pendent arm are absolutely essential
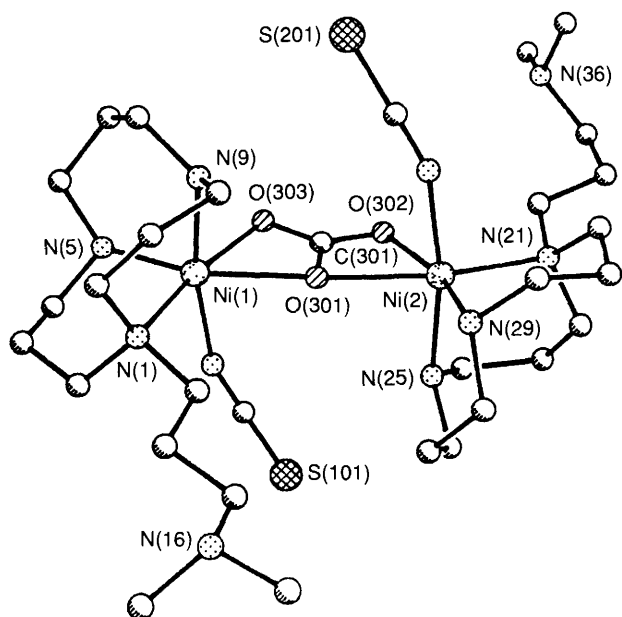

12N3   L¹   L²
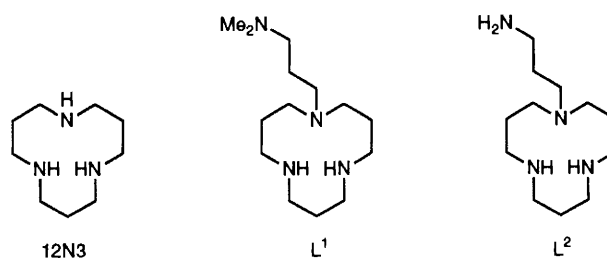
Fig. 1 The structure of the $[\{(HL^1)Ni(NCS)\}_2(CO_3)]^{2+}$ cation in $[\{(HL^1)Ni(NCS)\}_2(CO_3)](ClO_4)_2 \cdot 3H_2O$. Ligand atoms are numbered sequentially around the macrocyclic ring. Bond distances (Å) and angles (°) involving the µ-carbonato bridge are as follows: Ni(1)–O(301), 2.191(4); Ni(1)–O(303), 2.079(4); Ni(2)–O(301), 2.200(4); Ni(2)–O(302), 2.077(4); C(301)–O(301), 1.279(8); C(301)–O(303), 1.266(8); C(301)–O(303), 1.273(8); O(301)–Ni(1)–O(303), 61.6(2); O(301)–Ni(2)–O(302), 61.6(2); Ni(1)–O(301)–Ni(2), 174.1(2); Ni(1)–O(301)–C(301), 87.4(4); Ni(2)–O(301)–C(301), 86.7(3); Ni(1)–O(303)–C(301), 92.6(4); Ni(2)–O(302)–C(301), 92.5(4); O(301)–C(301)–O(302), 118.8(6); O(301)–C(301)–O(303), 118.1(6); O(302)–C(301)–O(303), 123.0(6).

for CO_2 uptake. Interestingly, Zn^{II} complexes of 12N3 and related pendent-arm ligands have been postulated as possible models for the active site in carbonic anhydrase.[5]

X-Ray crystallography† shows that in $[\{(HL^1)Ni(NCS)\}_2$-$(CO_3)](ClO_4)_2 \cdot 3H_2O$ the macrocyclic portion of the ligand coordinates facially to the octahedral Ni^{II} centre (Fig. 1). The pendent arm is protonated and does not coordinate; instead, coordination at each nickel(II) is completed by an *N*-bonded thiocyanate and a µ-bridging carbonate. Nickel–amine distances fall within the usual ranges, with those to the
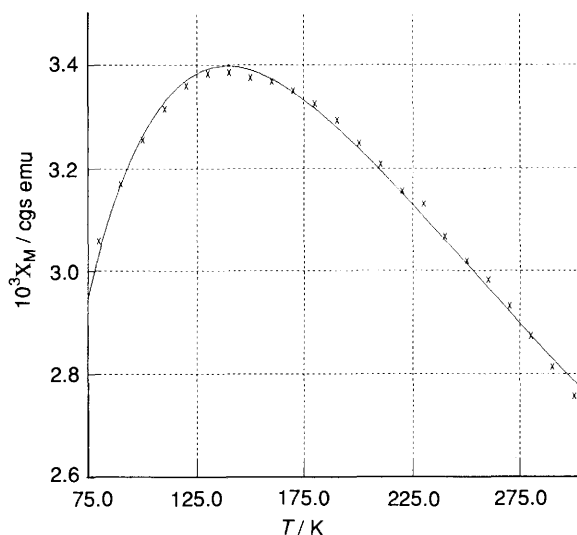
Fig. 2 Variation of the molar magnetic susceptibility (χ_M) with temperature for $[\{(HL^1)Ni(NCS)\}_2(CO_3)](ClO_4)_2 \cdot 3H_2O$ (×, exptl.; —, calc.)

tertiary nitrogens exceeding those to the secondary ring nitrogens. The N–Ni–N chelate angles within the macrocycle exceed 90° (average 96°), complementing the small chelate angle [61.6(2)° at both Ni^{II} centres] subtended by the carbonate. The thiocyanates bind *trans* to secondary ring N atoms, whilst the µ-O atom of the carbonato ligand opposes the tertiary N atom on Ni(2) and a secondary ring N atom on Ni(1). Bond lengths from the Ni atoms to the bridging O atom $[O_b = O(301)]$ of the µ-carbonato group (average 2.195 Å) exceed those to the other two O atoms $[O_a = O(302)$ and $O(303)]$, as is found in analogous Cu^6 and Rh^7 complexes. In addition, $C–O_a–M$ angles (average 93°) exceed $C–O_b–M$ ones (average 87°), whilst in the µ-carbonato group the $O_a–C–O_a$ angle (123°) exceeds the $O_a–C–O_b$ angles (average 118.5°). The µ-carbonate ion, the protonated pendent arm and the waters of crystallisation participate in an extended hydrogen-bonding network. Although bond distances and angles within the perchlorate counterions lie within normal ranges, the O atoms display large vibrational amplitudes as they do not participate in the hydrogen-bonding network.

The variation of molar magnetic susceptibility and magnetic moment for the dinickel complex in the temperature range 80 to 300 K (Fig. 2)‡ indicates a strong antiferromagnetic interaction. The closest fit to this data is obtained using eqn. (1), which corresponds to the intramolecular exchange between two $S = 1$ ions,[8] with $g = 2.00(2)$, an exchange constant $-2J = 94.6(4)$ cm^{-1} and a correction $N\alpha = 4.7(5) \times 10^{-4}$ cgs emu for temperature-independent paramagnetism. The value of g lies towards the low end of the range (2.14–2.46) previously observed in Ni^{II} dimers, whilst $N\alpha$ is somewhat larger than previously suggested (2.0–2.6 × 10^{-4} cgs emu).[9,10] The antiferromagnetic exchange constant exceeds by a factor of three the highest reported value for an *O*-bridged dinickel(II) dimer.

$$\chi_M = \frac{N_A\mu^2_B g^2}{kT} \frac{(e^{2J/kT} + 5e^{6J/kT})}{(1 + 3e^{2J/kT} + 5e^{6J/kT})} + N\alpha \qquad (1)$$

Although it is more common to include zero-field D and inter-dimer exchange $z'J'$ contributions in evaluating magnetic data for nickel dimers,[9] doubt has been cast on the

1703

validity of this treatment of powder data owing to the strong correlation between D and $z'J'$. In this complex the close fit of the data to eqn. (1) indicates that intra-dimer exchange dominates. Strong antiferromagnetic coupling in $[\{(HL^1)Ni(NCS)\}_2(CO_3)]^{2+}$ may be rationalised on the basis of a superexchange pathway in which the Ni^{II} d_{z^2} (magnetic) orbitals interact via the μ-carbonato O-bridge. This linear Ni–O–Ni linkage provides ideal geometry for the exchange, which in dicopper(II) complexes is known to result in diamagnetism.[6a] A complex formulated as a μ-hydroxo-bridged dinickel(II) dimer, $[\{(tren)NiOH\}_2OH]^+$ [tren = tris-(2-aminoethyl)amine], is also reported to be diamagnetic, presumably owing to superexchange.[11]

We thank the SERC for financial support and for provision of X-ray and NMR facilities. Support from the Atomic Energy Establishment (Winfrith) is also gratefully acknowledged.

References

1 N. W. Alcock, A. C. Benniston, P. Moore, G. A. Pike and S. C. Rawle, *J. Chem. Soc., Chem. Commun.*, 1991, 706.

2 S. C. Rawle, A. J. Clarke, P. Moore and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 2755.

3 P. W. N. M. van Leeuwen and W. L. Groenweld, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 145.

4 T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayishi, T. Sakurai and S. Yano, *Inorg. Chem.*, 1992, **31**, 1058.

5 E. Kimura, T. Shiota, T. Koike, M. Shiro and M. Kodama, *J. Am. Chem. Soc.*, 1990, **112**, 5805.

6 (a) M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, M. W. Rupich and K. O. Watkins, *Inorg. Chem.*, 1979, **18**, 2296; M. R. Churchill, G. Davies, M. A. El-Sayed and J. P. Hutchinson, *Inorg. Chem.*, 1983, **21**, 1002, A. R. Davis, F. W. B. Einstein, N. F. Curtis and J. W. L. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 6258; A. R. Davis and F. W. B. Einstein, *Inorg. Chem.*, 1980, **19**, 1203; (b) J. Sletten, H. Hope, M. Julve, O. Kahn, M. Verdauer and A. Dworkin, *Inorg. Chem.*, 1988, **27**, 542; N. Kitajima, K. Fujisawa, T. Koda, S. Hikichi and Y. Moro-oko, *J. Chem. Soc., Chem. Commun.*, 1990, 1357.

7 T. Yoshida, W. J. Youngs, T. Sakaeda, T. Ueda, S. Otsuka and J. A. Ibers, *J. Am. Chem. Soc.*, 1983, **105**, 6273.

8 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **58**, 203.

9 A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2884.

10 R. L. Lintvedt, L. L. Borer, D. P. Murtha, J. M. Kuszaj and M. D. Glick, *Inorg. Chem.*, 1974, **13**, 18.

11 H. B. Jonassen and V. V. Ramanujam, *J. Phys. Chem.*, 1959, **63**, 411.