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Attempted Syntheses of Transition Metal and Lanthanide (Dialkylamino)squarates. The Hydrolysis Problem

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Reaction of 1-amino-2-methoxycyclobutenedione with $M(NO_3)_2 \cdot xH_2O$ (M = Mn, Co, Ni, Cu, Zn) in aqueous solution results in the formation of the squarates $M(C_4O_4) \cdot 4H_2O$ and/or $M(C_4O_4) \cdot 2H_2O$ owing to the hydrolysis of both the methoxy and amino groups on the ligand. Similarly, reaction of this ligand with $M(NO_3)_3 \cdot 6H_2O$ (M = La, Eu, Gd, Tb) results in the formation of the respective lanthanide squarates. Buffering the reactant solutions at different pH's did not change the results and neither did using the alternative solvents methanol, ethanol, propan-1-ol, and acetonitrile. In previously reported reactions between 1-amino-2-methoxycyclobutenedione and 1-(dimethylamino)-2-methoxycyclobutenedione separately with $Pb(NO_3)_2$ under similar reaction conditions, the amino groups remained unhydrolyzed. The substituent amino groups also remain unhydrolyzed when these ligands are left to stand in aqueous solution in the absence of transition metal ions; only the methoxy group is hydrolyzed. 1-(Dimethylamino)-2-hydroxycyclobutenedione (**1**), formed from such a hydrolysis of 1-(dimethylamino)-2-methoxycyclobutenedione in aqueous solution, crystallizes in space group $P2_1/c$, with $a = 5.093(1)$ Å, $b = 8.331(1)$ Å, $c = 15.087(3)$ Å, $\beta = 95.12(1)°$, and $Z = 4$. However, attempts at complexation of the ligand with Mn(II) ions resulted in the formation of a mixture of the Mn(II) squarate $Mn(C_4O_4) \cdot 4H_2O$ and the salt $[Mn(H_2O)_6][HC_4O_3NH_2]_2 \cdot 2H_2O$ (**2**), in which the amino group remains intact. Compound **2** crystallizes in the tetragonal space group $P4_2/m$ with $a = 7.251(3)$ Å, $c = 15.979(8)$ Å, and $Z = 2$. If tetraethylammonium aminosquarate is used instead of 1-amino-2-methoxycyclobutenedione, both $[Co(C_4O_4)(H_2O)_4]$ and $[Co(C_4O_4)(H_2O)_2]$ are formed on reaction with $Co(NO_3)_2 \cdot 6H_2O$. Hydrolysis of the amino group also occurs when the higher homologue 1-(dimethylamino)-2-methoxycyclobutenedione is reacted with $Co(NO_3) \cdot 6H_2O$, but only $[Co(C_4O_4)(H_2O)_2]$ is formed. $[Co(C_4O_4)(H_2O)_2]$ crystallizes in the space group $Pn\bar{3}n$ with $a = 16.256(1)$ Å and $Z = 24$ and is isomorphous with $[Co(C_4O_4)(H_2O)_2] \cdot 0.33H_2O$, which has been reported previously. Evidence suggests that the hydrolysis of the dialkylamino substituents in the 1-(dialkylamino)-2-methoxycyclobutenediones is apparently mediated by the transition and lanthanide metals. The use of the hydrolysis of the amino group in 1-dialkylamino derivatives of squaric acid as a convenient synthetic tool is discussed.

Introduction

Reactions of aqueous solutions of lead nitrate with 1-dialkylamino derivatives of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid) produced a series of polymeric complexes with the lead atoms linearly arranged when viewed along the polymer chains.[1] Neighboring lead atoms in these compounds are oxo-bridged, and the ligand complexes in a μ-1,2 fashion in each case. A number of transition metal squarate complexes containing the squarate ion in a similar coordination mode show significant antiferromagnetic interactions while such interactions in complexes with the squarate ion μ-1,3 coordinated are negligible.[2−7] Molecular orbital calculations suggest that the lowering of the symmetry of the ion from D_{4h} in the μ-1,3-bridged complexes to C_{2v} in complexes where it is μ-1,2 coordinated is responsible for the energies of the metal and ligand orbitals being closer, with a consequential improvement

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(1) (a) Narinesingh, D.; Ramcharitar, N.; Hall, L.; Williams, D. J. *Polyhedron* **1994**, *13*, 45. (b) Hall, L. A.; Williams, D. J.; Menzer, S.; White, A. J. P. *Inorg. Chem.* **1997**, *36*, 3096.

(2) Frankenbach, G. M.; Beno, M. A.; Kini, A. M.; Williams, J. M.; Welp, U.; Thompson, J. E.; Whangbo, M.-H. *Inorg. Chim. Acta* **1992**, *192*, 195.

(3) Xanthopoulos, C. E.; Sigalas, M. P.; Katsoulos, G. A.; Tsipis, C. A.; Hadjikostas, C. C.; Terzis, A.; Mentzafos, M. *Inorg. Chem.* **1993**, *32*, 3743.

(4) Khan, M. I.; Chang, Y.-D.; Chen, Q.; Salta, J.; Lee, Y.-S.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 6340.

(5) Hilbers, M.; Meiwald, M.; Mattes, R. *Z. Naturforsch.* **1996**, *51B*, 57.

(6) Trombe, J.-C.; Petit, J.-F.; Gleizes, A. *New J. Chem.* **1988**, *12*, 197.

(7) Solans, X.; Aguilo, M.; Gleizes, A.; Faus, J.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, *29*, 775.

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in the efficiency of metal−ligand overlap.[3,8] Exchange between metal and ligand is therefore facilitated. It was envisaged that polymeric transition metal and lanthanide complexes with the monosubstituted squarate ligand μ-1,2 coordinated and having structural characteristics similar to those of the lead (dialkylamino)squarates should also show antiferromagnetism and properties such as molecular magnetism, semiconduction, and other phenomena associated with or dependent upon such characteristics.[9−18] Any extended delocalization along the polymer chains in such complexes should enhance their potential for electron conduction and magnetic exchange. It was also assumed that the heavier transition and lanthanide metals with their relatively large ionic radii and ability to show large coordination numbers would more closely approximate the behavior of lead and as a result produce analogous compounds. Therefore, we decided to attempt the synthesis of selected lanthanide complexes with the 1-(dialkylamino)squarate ligands. It was also assumed that these ligands would show a diversity of coordination modes similar to those observed for the squarate ion in the lanthanide squarates synthesized by Trombe et al.[19,20] and that this diversity would prove advantageous with respect to the achievement of our goals. We also decided to attempt the synthesis of a few first-row transition metal complexes as well, despite their significantly smaller ionic radii and lower coordination numbers. The synthesis of the latter was done in order to obtain a more complete understanding of the complexing properties of the 1-dialkylamino derivatives of squaric acid. For example, comparisons of the C−C bond lengths of the ligand ring (and assessment of multiple-bond localization) can be made with respect to first-row transition metal complexes since the bond lengths in such complexes can be determined with greater accuracy than would be possible for complexes of heavier metals. Multiple-bond localization has been shown to play an important role in antiferromagnetic coupling.[3,4] In addition, we decided to investigate ring substituents other than the dialkylamino ones in order to ascertain the effects, if any, of varying the substituents on the structural, chemical, and other properties of the complexes formed when these ligands are reacted with transition and lanthanide metals.

This paper is one of a series which describes the attempted synthesis and characterization of a number of first-row transition and lanthanide metal complexes of monosubstituted squarate ligands.

Experimental Section

Preparation of Ligands. 1-Amino-2-methoxyclobutenedione was prepared according to the method of Cohen and Cohen.[21]

1-Amino-2-hydroxycyclobutenedione. 1-Amino-2-methoxycyclobutenedione was dissolved in water and the solution allowed to stand until the hydrolysis of the methoxy group was complete as evidenced by no further changes in the pH of the solution. The solution was then left to stand at ambient conditions until crystallization was complete. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.1 (s, 2H), δ 10.55 (s, 1H).

Tetraethylammonium Aminosquarate. A 17.7 mL (1.77×10^{-2} mol) portion of tetraethylammonium hydroxide was added dropwise to 50 mL of an equimolar solution of 1-amino-2-hydroxycyclobutenedione. The pH was not allowed to exceed 6.0 during the addition. The mixture was evaporated to dryness on a rotary evaporator, and the crude product was recrystallized from MeCN. ^{1}H NMR (80 MHz, DMSO-d_6): δ 1.08 (t, J = 6.7 Hz, 3H), 1.15 (t, J = 6.7 Hz, 6H), 1.26 (t, J = 6.7 Hz, 3H), 3.20 (q, J = 6.7 Hz, 8H), 4.20 (s, 2H).

1-(Dimethylamino)-2-methoxycyclobutenedione. This was prepared according to the procedure previously described.[1b]

1-(Dimethylamino)-2-hydroxycyclobutenedione. This was prepared by dissolving 1-(dimethlyamino)-2-methoxycyclobutenedione in water and allowing the solution to stand until there was no further change in the pH of the solution. The mixture was then allowed to stand at room temperature until crystallization was complete. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.15 (s, 6H), δ 7.7 (s, 1H).

Preparation of the Complexes. $CoC_4O_4{\cdot}2H_2O$. A 125 mL portion of an aqueous solution of tetraethylammonium aminosquarate (0.20 g, 7.41×10^{-4} mol) was mixed with 125 mL of an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.43 g, 1.48×10^{-3} mol). The mixture was then filtered, and the filtrate was allowed to evaporate slowly until crystal formation was complete.

$Co(C_4O_4){\cdot}2H_2O$. Pink cubes were obtained. Anal. Calc for $C_4H_4O_6Co$: C, 23.21; H, 1.95; Co, 28.47. Found: C, 23.28; H, 2.18; Co, 28.61.

$[Mn(H_2O)_6][HC_4O_3NH_2]_2{\cdot}2H_2O$. An aqueous solution of $Mn(NO_3)_2{\cdot}6H_2O$ (0.23 g, 7.87×10^{-4} mol) was mixed with an equimolar solution of 1-amino-2-methoxycyclobutenedione in water. The mixture was then filtered, and the filtrate was allowed to evaporate slowly until crystal formation was complete.

$[Mn(H_2O)_6][HC_4O_3NH_2]_2{\cdot}2H_2O$. Clear, rhombus-shaped rods were obtained. Only a few crystals of this salt were formed (the product was predominantly $[Mn(C_4O_4)(H_2O)_4]$), and therefore no elemental analyses were done.

Elemental Analyses. C, H, N analyses were performed by MEDAC Limited, Brunel University, Uxbridge, Middlesex, U.K. The Co and Mn analyses were done by flame atomic absorption spectrophotometry using a Unicam 929 atomic absorption spectrometer.

NMR Spectra. The NMR spectra were recorded on a Bruker 80, a Varian Gemini 200, a Varian XL-400, and a Bruker DRS 400 spectrometer.

Crystallographic Analyses. Crystallographic data for $[(CH_3)_2NC_4O_3H]$ (**1**) and $[Mn(H_2O)_6][HC_4O_3NH_2]_2{\cdot}2H_2O$ (**2**) are summarized in Table 1. Data for **1** were collected on an Enraf-Nonius CAD4-U diffractometer (Cu radiation).[22] The data were processed using the Enraf-Nonius MolEN package;[23] the structure was solved by direct methods (SHELXS-86).[24] Full-matrix least-squares refinement was carried out using the Oxford University CRYSTALS-PC system.[25] All

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(8) Castro, I.; Sletten, J.; Calatayud, M. L.; Julve, M.; Cano, J.; Lloret, F.; Caneschi, A. *Inorg. Chem.* **1995**, *34*, 4903.

(9) Habenschuss, M.; Gerstein, B. C. *J. Chem. Phys.* **1974**, *61*, 852.

(10) Collman, J. P.; McDevitt, J. T.; Yee, G. T.; Leidner, C. R.; McCullough, L. G.; Little, W. A.; Torrance, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4581.

(11) Robl, C.; Weiss, A. *Z. Naturforsch.* **1986**, *41B*, 1485.

(12) Collman, J. P.; McDevitt, J. T.; Leidner, C. R.; Yee, G. T.; Torrance, J. B.; Little, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 4606.

(13) Chen, Q.; Liu, S.; Zubieta, J. *Inorg. Chim. Acta* **1989**, *164*, 115.

(14) Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. *T. Am. Chem. Soc.* **1992**, *114*, 6974.

(15) Mallah, T.; Thiebaut, S.; Verdaguer, M.; Veillet, P. *Science*, **1993**, *262*, 1554.

(16) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397.

(17) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701.

(18) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.* **1997**, *36*, 3440.

(19) Petit, J.-F.; Gleizes, A.; Trombe, J.-C. *Inorg. Chim. Acta.* **1990**, *167*, 51.

(20) Trombe, J.-C.; Petit, J.-F, Gleizes, A. *Inorg. Chim. Acta*. **1990**, *167*, 69.

(21) Cohen, S.; Cohen, S. G. *J. Am. Chem. Soc.* **1956**, *88*, 1533.

(22) Straver, L. H. *CAD4-EXPRESS*; Enraf-Nonius: Delft, The Netherlands, 1992.

(23) Fair, C. K. *MolEN: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(24) Robinson, W. T.; Sheldrick, G. M. In *Crystallographic Computing 4. Techniques and New Technologies*; Isaccs, N. W., Taylor, M. R., Eds.; Oxford University Press: Oxford, U.K., 1988; pp 366−377.

(25) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *Crystals Issue 10*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1996.

Table 1. Crystallographic Data for [$(CH_3)_2NC_4O_3H$] (**1**) and [$Mn(H_2O)_6$][$HC_4O_3NH_2$]$_2$·$2H_2O$ (**2**)

	1	**2**
empirical formula	$C_6H_7NO_3$	$C_8H_{22}N_2O_{14}Mn$
a, Å	5.093(1)	7.251(3)
b, Å	8.331(1)	
c, Å	15.087(3)	15.979(8)
β, deg	95.12(1)	
V, Å^3	637.7(2)	840.2(6)
Z	4	2
fw	141.13	424.21
space group	$P2_1/c$ [C^5_{2h}; No. 14]	$P4_2/m$ [C^2_{4h}; No. 84]
T, °C	21	20
λ, Å	1.541 78	0.710 73
ρ_{calc}, g cm^{-3}	1.470	1.677
μ, cm^{-1}	0.975	0.862
transm factors	0.959−0.996	
R^a	0.0347	0.0419
$R_w{}^b$	0.0425	0.0947

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$.

non-hydrogen atoms were refined using anisotropic displacement parameters; H atoms were refined using isotropic displacement parameters. Drawings were produced using the Oxford University program CAMERON.[26] A full report on structure **1** is available as a CIF file (Supporting Information).

Data for the structure of [$Mn(H_2O)_6$][$HC_4O_3NH_2$]$_2$·$2H_2O$ (**2**) were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects. The structure was solved using the SHELXTL-PC[27] package. Refinement was performed by full-matrix least-squares calculations on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o{}^2) + (0.045P)^2 + 0.72P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. Hydrogen atoms were refined with isotropic thermal parameters.

Results and Discussion

Attempts at synthesizing Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-amino-2-methoxycyclobutenedione resulted in the hydrolysis of both the methoxy and amino substituents on the ligand and the formation of the tetrahydrates $M(C_4O_4)$·$4H_2O$ and/or the dihydrates $M(C_4O_4)$·$2H_2O$ (M = Co, Ni, Cu, Zn), which are the identical complexes produced by reacting squarate salts with the respective metal nitrates in aqueous solution.[28] In addition, La, Eu, Gd, and Tb squarates were produced when their respective nitrates were reacted with the ligand, indicating that hydrolysis of the methoxy and amino groups also occurred in these syntheses. The La squarate is isomorphous with the Nd analogue, the Eu squarate is identical to [$Eu(H_2O)_4$]$_2$(C_4O_4)$_3$ synthesized by Petit et al., while the Gd and Tb squarates are isomorphous with this same Eu squarate.[19] The hydrolysis of the methoxy group was expected since it was previously observed in the preparation of a series of lead(II) 1-(dialkylamino)squarates, but the hydrolysis of the amino group was unexpected.[1]

Similar results were obtained even when the syntheses were carried out in other solvents such as methanol, ethanol, propan-1-ol, and acetonitrile where reactant solubilities permitted. Neither buffering the reactant solutions nor using 1-(dimethylamino)-2-cyclobutenedione, the next higher homologue, had any effect on the hydrolysis.

Manganese(II), however, gave a mixture of manganese(II) squarate and small quantities of a salt which contained [$Mn(H_2O)_6$]$^{2+}$ ions balanced by pairs of $NH_2C_4O_3H^-$ anions. Thus, the only reaction where the amino group appeared in the product was one in which complexation did not occur.

Cobalt(II) gave different products when reacted separately with 1-amino-2-methoxycyclobutenedione and tetraethylammonium aminosquarate, respectively, in aqueous solution. Cobalt(II) squarate tetrahydrate, CoC_4O_4·$4H_2O$, was the only product obtained with 1-amino-2-methoxycyclobutenedione. However, when the reaction was repeated using tetraethylammonium aminosquarate, crystals of two different morphologies were formed. The two different crystalline forms were determined to be cobalt(II) squarate tetrahydrate, CoC_4O_4·$4H_2O$, and cobalt(II) squarate dihydrate, CoC_4O_4·$2H_2O$, respectively, by single-crystal X-ray crystallography. Further, when the synthesis was done with 1-(dimethylamino)-2-methoxycyclobutenedione, CoC_4O_4·$2H_2O$ was again the sole product. These two cobalt complexes have different structures, both of which have been previously determined. The fact that two products are formed when tetraethylammonium aminosquarate is used in the preparation of the cobalt complex, as opposed to one when 1-amino-2-methoxycyclobutenedione is used, is assumed to be due to the fact that the former ligand is able to complex more quickly than the latter. In the case of the latter, the methoxy group has to hydrolyze first before complexation occurs, the extra time required apparently facilitating the formation of the chain squarates $M(C_4O_4)$·$4H_2O$. The tetraethylammonium aminosquarate, on the other hand, should complex immediately and afford the formation of both the chain squarate and the 3-dimensional cage structure. The formation of a single product (CoC_4O_4·$2H_2O$) when 1-(dimethylamino)-2-methoxycyclobutenedione was used is assumed to be due to a more rapid hydrolysis of the dimethylamino substituent after complexation.

These were interesting results which we decided to investigate further in order to ascertain the factors responsible for the hydrolysis of the amino group under certain conditions. These results are now analyzed and discussed.

The substituent amino groups in both 1-amino-2-methoxycyclobutenedione and 1-(dimethylamino)-2-methoxycyclobutenedione are resistant to hydrolysis in aqueous solution in the absence of transition metal ions as evidenced by NMR spectroscopy. Analysis of the NMR spectrum of the 1-amino-2-methoxycyclobutenedione ligand showed the presence of both methoxy and amino groups (Figure 1a). However, reflux of an aqueous solution of this ligand for 2 h gave nearly a quantitative yield of a product whose NMR spectrum, obtained from a solution of the sample of the ligand in dry DMSO-d_6, was compatible with that expected for 1-amino-2-hydroxycyclobutenedione (δ 2.1, NH_2 protons; δ 10.6, hydroxy proton). Thus, only the methoxy group was hydrolyzed, leaving the amino group in tact. When DMSO-d_6 containing moisture is used, the amino group on the ligand apparently becomes protonated due to interaction with the moisture in the solvent. The deshielding observed in the spectrum (δ 7.1) is consistent with the protonation of the amino group while the resulting formation of an sp^3-hybridized N results in $^{14}N-^1H$ coupling (Figure 2a: note the three peaks which integrate in a 1:1:1 ratio, $J = 51$ Hz).[29]

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(26) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1996.

(27) Sheldrick, G. M. *SHELXTL-PC*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(28) Weiss, A.; Riegler, E.; Alt, I.; Bohme, H.; Robl, C. *Z. Naturforsch.* **1986**, *41B*, 18.

(29) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy: A Guide for Chemists*; Oxford University Press: Oxford, U.K., 1987; pp 216, 217.

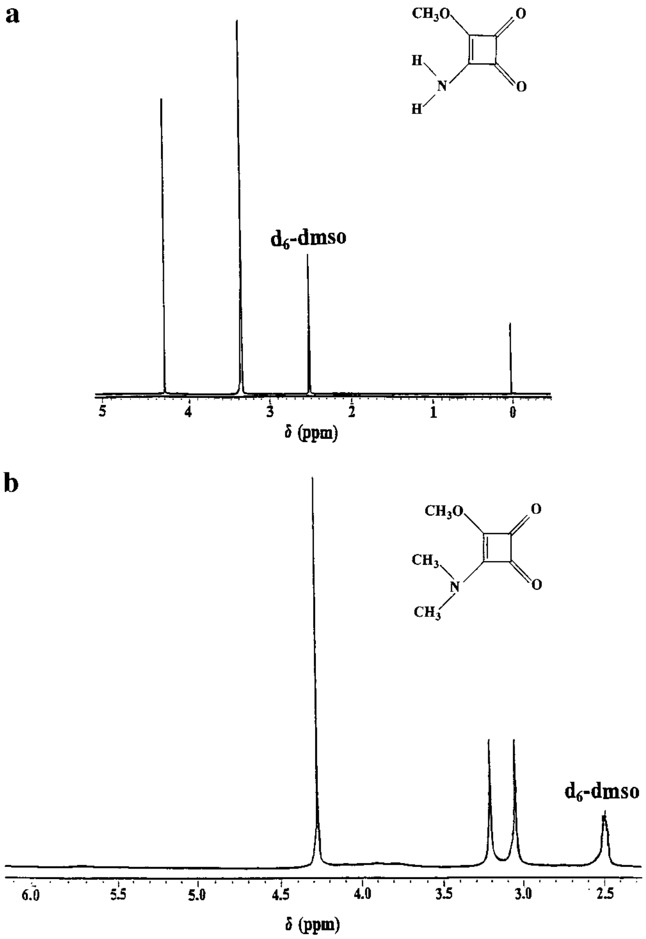

Figure 1. (a) NMR spectrum of 1-amino-2-methoxycyclobutenedione. (b) NMR spectrum of 1-(dimethylamino)-2-methoxycyclobutenedione.

The unexpected resistance to hydrolysis of the amino group in the ligand 1-amino-2-hydroxycyclobutenedione in aqueous solution is most likely a result of the resonance stabilization of the aminosquarate ion. The amino group in this ion is coplanar with the C_4-cycle (the plane formed by the NH_2 group deviates by 0.066 Å from the plane of the C_4-cycle), which facilitates the migration of the N lone pair of electrons onto the ring as evidenced by the short C−N bond (1.319(5) Å) (Figure 3). This contributes to the resonance stabilization of the ion, which has dimensions that are similar to those of the squarate ion, which is known to be significantly resonance stabilized.

The dimethylamino substituent on the 1-(dimethylamino)-2-methoxycyclobutenedione ligand (NMR spectrum in Figure 1b) was also used in attempted syntheses of transition metal complexes. When an aqueous solution of this ligand is allowed to stand, the ^{1}H NMR spectrum of the resulting product shows evidence of the dimethylamino group but not of the methoxy group (δ 3.2, CH_3 protons; δ 7.8, hydroxy proton). Again, the ligand exists in the protonated form in DMSO-d_6 that contains moisture. The methyl groups on the nitrogen atoms are apparently in slightly different electronic environments, and this, in addition to $^1H-^{14}N$ coupling ($J = 30$ Hz, Figure 2b),[29] causes the H signal to appear as two sets of multiplets (δ 7.60). However, hydrolysis of not only the methoxy substituent but also the amino substituent occurs when 1-amino-2-methoxycyclobutenedione and 1-(dimethylamino)-2-methoxycyclobutenedione, respectively, are reacted with transition and lanthanide metals.

X-ray structural and NMR data provide evidence for the existence of canonical forms of these ligands, resulting from the migration of the lone pair of electrons on the nitrogen atom onto the C_4-rings. Such canonical forms should be susceptible to hydrolysis from nucleophilic attack by water molecules at the carbon atom to which the amino groups are attached as expected for any analogous enamine. The proton NMR spectrum of the ligand 1-(dimethylamino)-2-methoxycyclobutenedione shows two different sets of equivalent peaks for the methyl protons on the N, indicating that these protons exist in different electronic environments (Figure 1b). This suggests that there

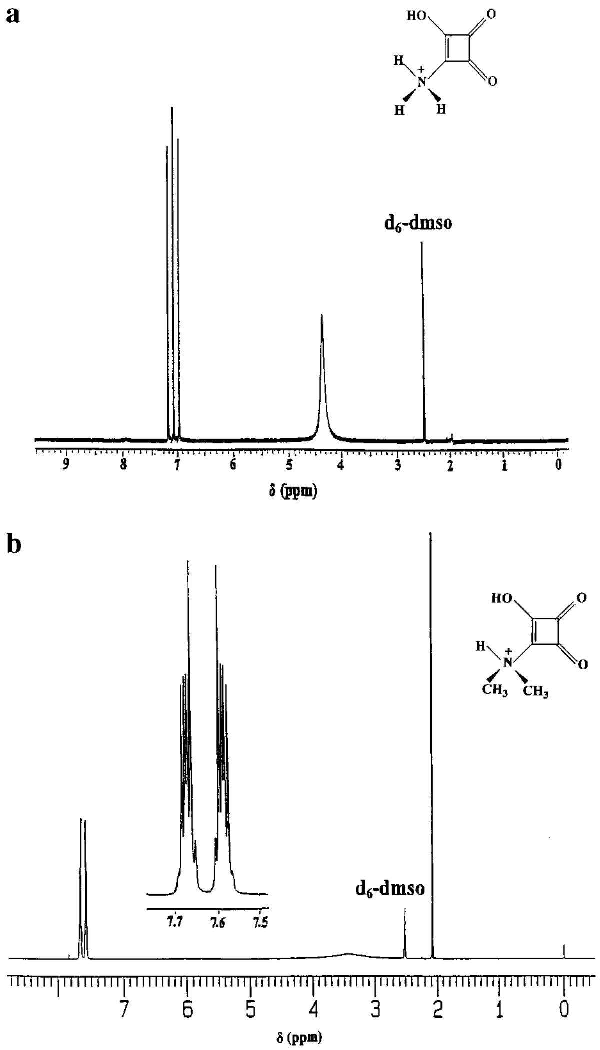

Figure 2. (a) NMR spectrum of protonated 1-amino-2-hydroxycyclobutenedione. (b) NMR spectrum of protonated 1-(dimethylamino)-2-hydroxycyclobutenedione.

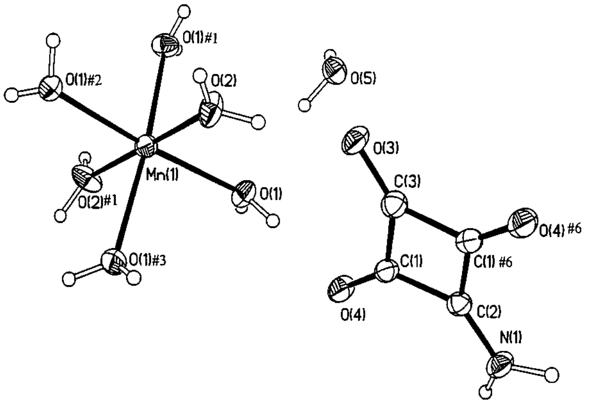

Figure 3. Molecular structure of $[Mn(H_2O)_6][HC_4O_3NH_2]_2{\cdot}2H_2O$ (**2**) (50% thermal vibrational ellipsoids).

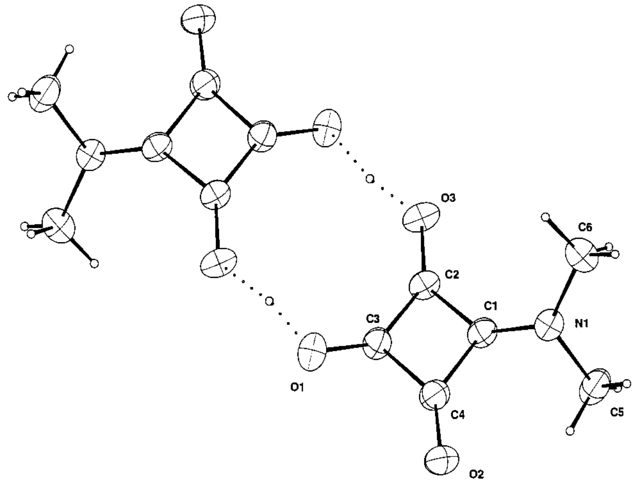

Figure 4. Molecular structure of 1-(dimethylamino)-2-hydroxycyclobutenedione (**1**) (50% thermal vibrational ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(CH_3)_2NC_4O_3H]$ (**1**)

O(1)−C(3)	1.276(2)	C(2)−C(3)	1.427(2)
O(2)−C(4)	1.216(2)	C(3)−C(4)	1.477(2)
O(3)−C(2)	1.280(2)	C(5)−N(1)	1.462(2)
C(1)−C(2)	1.441(2)	C(6)−N(1)	1.462(2)
C(1)−C(4)	1.489(2)	O(1)−H(1)	1.27(3)
C(1)−N(1)	1.300(2)	O(3)−H(1)	1.23(3)
C(1)−C(2)−C(3)	91.37(9)	O(3)−C(2)−C(1)	131.4(1)
C(1)−C(4)−C(3)	87.55(9)	O(3)−C(2)−C(3)	137.2(1)
C(2)−C(1)−C(4)	90.05(9)	C(1)−N(1)−C(5)	121.3(1)
C(2)−C(3)−C(4)	91.02(9)	C(1)−N(1)−C(6)	121.8(1)
C(2)−C(1)−N(1)	135.1(1)	C(5)−N(1)−C(6)	116.9(1)
C(4)−C(1)−N(1)	134.9(1)	O(1)−H(1)−O(3)	167.6(3)

is restricted rotation about the C−N bond, which is consistent with a significant amount of double-bond character in this bond due to migration of the nitrogen lone pair. Evidence for a similar electron migration in 1-(dimethylamino)-2-hydroxycyclobutenedione (**1**), obtained from the hydrolysis of the methoxy compound in aqueous solution, is provided by X-ray structural data. The C−N bond connecting the dimethylamino substituent to the C_4-cycle (1.300(1) Å) in **1** is almost as short as a carbon−nitrogen double bond[30] (Figure 4, Table 2) while the C−N bonds connecting the N atom to the methyl groups are both 1.462(2) Å, which is the length of a normal C−N single bond. The electron migration is again facilitated by the coplanarity of the amino substituent with the C_4-cycle; the angle between the C_4-plane and the $N-C_2$ plane of the dimethylamino group is 2.40° (Figure 4). This electron migration continues within the C_4-ring as indicated by the C−C and C−O bond lengths in this structure which are compatible with the bond lengths expected for the canonical form of the ligand consistent with this electron migration scheme. Additionally, this canonical form should be stabilized by the withdrawal of electron density into the metal orbitals when the ligand complexes. Further, the hydrolysis of the dimethylamino substituent will be facilitated by the coplanarity of the methyl groups with the squarate ring, which allows nucleophilic attack from both above and below the ring. Inspection of Figure 4 and Table 2 also reveals that the hydroxyl proton is involved in a very strong hydrogen bond,[31] O(1)−H(1)···O(3) $[\bar{x}, \bar{y}, 1 - z]$ (O(1)···O(3) = 2.481 Å; O(1)···H(1)···O(3) = 168°). Similarly, the analogous canonical form of the ligand 1-amino-2-hydroxycyclobutenedione will also be susceptible to nucleophilic attack.

It is expected that at lower pH's the 1-(dialkylamino)squarate ligands will exist predominantly in protonated forms on the basis of the evidence provided by the NMR data. This will also make them susceptible to nucleophilic attack in a manner similar to that described before.

We believe that the (dialkylamino)squarate ligands actually form complexes with the transition and lanthanide metals initially with the subsequent hydrolysis of the amino substituent being mediated by the metals upon complexation. It appears that the size and charge of the metal ions in addition to the energies of the metal orbitals used in bonding with the ligand are important with respect to the hydrolysis of the substituent occurring. Thus, in instances when the energies of the bonding metal orbitals are comparable to those of the ligand orbitals, the resulting efficiency of the orbital overlap facilitates electron transfer into the metal orbitals, which further sensitizes the substituent group to hydrolysis. Xanthopoulos et al.[3] showed that when the symmetry of the squarate ring is lowered from D_{4h} to C_{2v}, there is greater interaction of the metal and ligand orbitals (vide supra). The presence of the dialkylamino substituent on the C_4-ring automatically confers C_{2v} symmetry on these ligands, which apparently makes the overlap between metal and ligand orbitals efficient.

For purposes of comparison, it must be remembered that according to Hall et al.[1a,b] the hydrolysis of the amino groups does not occur during the preparation of three Pb complexes with different monosubstituted 1-(dialkylamino) derivatives of squaric acid although these were prepared under conditions similar to those used in the attempted syntheses of the first row transition and lanthanide complexes discussed in this paper. We speculate that in the Pb complexes the large size of the metal ion and the unavailability of d orbitals of appropriate energy to accommodate the electrons from the ring prevent electron migration and the resultant sensitization of the amino substituent to hydrolysis.

Structure of $[Co(C_4O_4)(H_2O)_2]$. Our experiments indicate that $[Co(C_4O_4)(H_2O)_2]$ is identical to $[Co(C_4O_4)(H_2O)_2]\cdot 0.33H_2O$ reported by Lee et al.[32] and isomorphous with the complexes $(MC_4O_4\cdot 2H_2O)_3\cdot CH_3COOH\cdot H_2O$ (M = Ni, Zn) reported by Weiss et al.[33] This complex crystallizes in the cubic system, space group $Pn\bar{3}n$, with $a = 16.256(1)$ Å (cf. 16.260(4) for the Zn complex). We collected a partial data set for the complex; the data were used to confirm the isomorphous nature of the structures ($R = 0.049$ for 258 reflections). As in the structures reported by Weiss et al., the complex consists of a 3-dimensional framework with each squarate ligand complexing in a tetrakismonodentate fashion to each of four Co atoms. The Co center is octahedrally coordinated, with two trans-aqua ligands completing the six-coordination. The compound was not analyzed further to determine the nature of any occluded solvent. Weiss et al.[33] were unable to locate occluded solvent by X-ray analysis and relied on elemental analysis for the complete unit cell information.

Structure of $[Mn(H_2O)_6][HC_4O_3NH_2]_2\cdot 2H_2O$ (2). The X-ray analysis of the salt (**2**) shows the Mn atom surrounded by a distorted octahedral array of aqua ligands (Figure 3). The deviation from the ideal O−Mn−O angle of 90° is close to 5°. Two of the six Mn−O bonds have lengths of 2.101(4) Å and are significantly shorter than the rest (2.218(2) Å, Table 3). Hydrogen-bonding interactions appear to be responsible for the distortion; each H atom on the oxygen atoms O(2) and O(2)#1

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[30] Mills, I. M.; Thompson, H. W. *Trans. Faraday Soc.* **1954**, *50*, 1270.

[31] Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

[32] Lee, C.-R.; Wang, C.-C.; Wang, Y. *Acta Crystallogr.* **1996**, *B52*, 966.

[33] (a) Weiss, A.; Riegler, E.; Robl, C. *Z. Naturforsch.* **1986**, *41B*, 1329. (b) Weiss, A.; Riegler, E.; Robl, C. *Z. Naturforsch.* **1986**, *41B*, 1333.

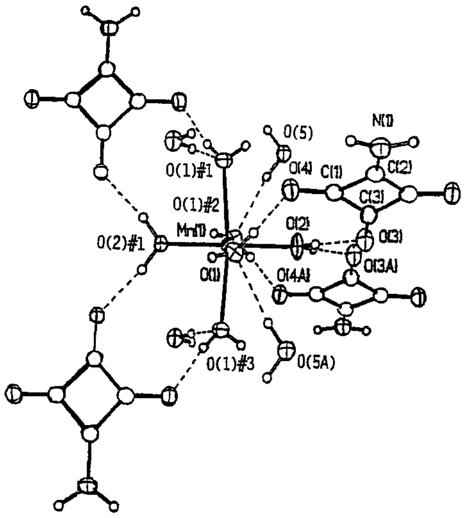

Figure 5. Part of the hydrogen-bonded network of **2**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mn(H_2O)_6][HC_4O_3NH_2]_2 \cdot 2H_2O$ (**2**)

Mn(1)−O(2)	2.101(4)	C(1)−C(2)	1.445(4)
Mn(1)−O(1)	2.218(2)	C(1)−C(3)	1.466(4)
O(3)−C(3)	1.248(4)	O(4)−C(1)	1.253(4)
N(1)−C(2)	1.319(5)		
O(2)−Mn(1)−O(2)#1	180.0	O(2)#1−Mn(1)−O(1)#2	94.80(7)
O(1)#3−Mn(1)−O(1)#1	170.4(2)	O(1)−Mn(1)−O(1)#1	90.401(12)
O(2)#1−Mn(1)−O(1)#3	85.20(7)		

is hydrogen-bonded to an O atom on a nearby aminosquarate ion. However, the H-bonding involving the other four aqua ligands is more complicated. In addition to the hydrogen atoms from these four aqua ligands being H-bonded to oxygen atoms on aminosquarate ions, their oxygen atoms are also H-bonded to nearby molecules of water of crystallization in the lattice (Figure 5).

The ring C−C bonds of the C_4-cycle in the aminosquarate ion in $[Mn(H_2O)_6][HC_4O_3NH_2]_2 \cdot 2H_2O$ **(2)** are only marginally different in bond length (1.445(4) and 1.466(4) Å) while those of the C_4-cycle in (dimethylamino)squarate differ in length by as much as 0.06 Å (Tables 2 and 3). The analogous bond lengths in the squarate ion in the compound $Cr(C_4O_4)_{3/2} \cdot 7H_2O$ are 1.457(4) and 1.470(4) Å.[34] The C−O bond lengths in **2** and $Cr(C_4O_4)_{3/2} \cdot 7H_2O$ are comparable.

Although the hydrolysis of the amino substituents prevents the preparation of transition metal (dialkylamino)squarate complexes under conditions similar to those used in the preparation of analogous lead 1-(dialkylamino)squarates, it may be used as a convenient synthetic tool. X-ray-quality crystals of metal squarates are often not easily unobtainable by reacting squaric acid with the appropriate metal salts, mainly due to the low solubility of a number of transition metal squarates, which results in the rapid precipitation of product in powder form. However, the use of either the appropriate 1-(dialkylamino)-2-alkoxybutenediones or the tetraethylammonium (dialkylamino)-squarate salts expands the range of solvents and reaction conditions, thus facilitating the preparation of good-quality crystals. Apparently the time taken for the hydrolysis to occur provides better conditions for proper crystal growth.

When monosubstituted squarate ligands with substituents that are not hydrolyzable are reacted with transition and lanthanide metals, a wide variety of novel complexes are produced. These complexes are to be reported in other publications.

Conclusions

The reaction of 1-(dialkylamino)squarate ligands with small cations results in the hydrolysis of the dialkylamino groups on complexation and the formation of the metal squarate. However, this hydrolysis can be effectively used in the syntheses of crystals of transition metal squarate complexes that are difficult to achieve with neat squaric acid.

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Supporting Information Available: CIF files containing data for the structures of **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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(34) (a) Chesick, J. P.; Doany, F. *Acta Crystallogr.* **1981**, *B37*, 1076. (b) Robl, C.; Weiss, A. *Z. Naturforsch.* **1986**, *41B*, 1485. (c) Robl, C.; Weiss, A. *Z. Naturforsch.* **1986**, *41B*, 1490.