were made anisotropic. The thermal parameters were quite large. The tetraethylammonium cations were disordered, and here the non-hydrogen atoms were treated isotropically. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. All refinements were performed by full-matrix least-squares procedures. The highest residual was 0.34 e Å^{-3}. Calculations were done on a MicroVAX II computer with the programs of SHELXTL-PLUS.[26] Significant crystal data are listed in Table II. Atomic coordinates are collected in Table III.

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Supplementary Material Available: Complete atomic coordinates (Table SI), bond distances (Table SII) and angles (Table SIII), anisotropic thermal parameters (Table SIV), and hydrogen atom positional parameters (Table SV) for $[Et_4N]_2[Ni_2(SEt)_2(CS_3)_2]$ (3 pages); a listing of observed and calculated structure factors for the above complex (7 pages). Ordering information is given on any current masthead page.

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Spontaneous Fixation of Carbon Dioxide in Air by a Nickel Diamine Complex: Synthesis and Characterization of a Trinuclear Nickel(II) Complex with a Novel Hydrogen Bonding System around a Carbonate Ligand

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The nickel(II) complex of *N,N*-dimethylethylenediamine (*N,N*-Me$_2$en), $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ (**1**), in aqueous ethanol spontaneously adsorbed and fixed CO_2 in air to give a trinuclear nickel(II) complex, $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4](ClO_4)_4$ (**2**). The complex **2** crystallizes in the hexagonal system, space group $P6_3$, with $a = 25.824$ (7) Å, $c = 14.506$ (3) Å, and $Z = 6$. The structure was solved by direct methods and refined by least-squares techniques to a final R value of 0.065 for 2940 independent reflections with $F_o > 3\sigma(F_o)$. The absolute configuration was determined by the Bijvoet method. The complex cation is trinuclear, which is made up of three octahedral nickel(II) complexes, Λ-*cis*-(*O,O*)-$[Ni(N,N\text{-}Me_2en)_2(CO_3)]$ and Λ- and Δ-*cis*-(*O,O*)-$[Ni(N,N\text{-}Me_2en)(H_2O)_2]^{2+}$, joined by a novel hydrogen bonding network around the coordinating carbonate ligand. This planar hydrogen bonding system might stabilize the bidentate carbonate, resulting in the spontaneous fixation of CO_2 in air. When analogous diamines (*N,N'*-dimethylethylenediamine, *N,N*-diethylethylenediamine, *N*-methylethylenediamine, *N*-ethylethylenediamine) were used instead of *N,N*-Me$_2$en, no fixation of CO_2 was observed. The N-substituent of diamines is an important factors in determining the occurrence of CO_2 uptake.

Introduction

The chemistry of CO_2 has been the subject of considerable investigative attention for a variety of reasons including its potential as a C1 feedstock,[2] the increase in atmospheric CO_2 concentration,[3] and its possible use as a substrate for storing solar energy.[4] In this regard, the fixation of CO_2 under mild conditions by transition metal complexes and its conversion into useful chemical compounds are significant subjects in inorganic chemistry. A number of transition metal complexes containing CO_2[5-9] and their derivatives (carbonate,[10-12] alkyl carbonate,[13-15] carbamate[15,16]) have been prepared and characterized. However, most of these complexes were air-sensitive and not suitable for CO_2 fixation under atmospheric conditions. Thus far studies concerning spontaneous

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fixation of atmospheric CO_2 by transition metal complexes were very rare, because of their instability in air and the low concentration of atmospheric CO_2.

Kato and Ito have reported that zinc(II) tetraazacycloalkane complexes in methanol adsorbed CO_2 in air and fixed it as monoalkyl carbonate on the metal centers, in which the cavity size of macrocyclic ligands and their N-substituents influenced the efficient CO_2 uptake.[15] Recently, Kitajima and Moro-oka et al. demonstrated the spontaneous fixation of atmospheric CO_2 by a binuclear bis(μ-hydroxo)copper(II) complex of hydrotris(3,5-diisopropylpyrazol-1-yl)borate, in that CO_2 contamination in air was fixed as a bridging carbonate ligand between the two copper atoms.[17]

In the present study, we found that the nickel(II) complex of *N,N*-dimethylethylenediamine (*N,N*-Me_2en), $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ (**1**), spontaneously fixed CO_2 under atmospheric conditions. Here, we wish to describe this novel spontaneous fixation of CO_2 in air and an X-ray crystal structure of a trinuclear nickel(II) complex with a novel hydrogen bonding system around a carbonate ligand derived from this CO_2 fixation.

Experimental Section

Materials. All reagents were of the best commercial grade and were used without further purifications. The following abbreviations are used: *N,N*-Me_2en, *N,N*-dimethylethylenediamine; *N,N'*-Me_2en, *N,N'*-dimethylethylenediamine; *N,N*-Et_2en, *N,N*-diethylethylenediamine; *N*-Meen, *N*-methylethylenediamine; *N*-Eten, *N*-ethylethylenediamine.

Measurements. Visible and near-infrared absorption spectra (AB) were measured with a Hitachi Model 340 recording spectrophotometer. Infrared spectra were recorded as KBr pellets on a Shimazu IR-400 recording spectrophotometer.

Preparation of $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4](ClO_4)_4$ (2). Method 1. [*Caution! Complex **2** is explosive if the solid is heated directly.*] A 20-mL volume of aqueous ethanolic solution containing $[Ni(N,N\text{-}Me_2en)_3](ClO_2)_2$[18] was stirred at room temperature for 24 h under atmospheric conditions, and then its volume was reduced to yield blue crystals. The crystals were recrystallized from an ethanol–water solution and were collected, washed with ether, and dried in vacuo (yield 72%). Anal. Calcd for $C_{25}H_{80}N_{12}O_{23}Cl_4Ni_3$: C, 24.32; H, 6.53; N, 13.61; Cl, 11.48. Found: C, 23.75; H, 6.30; N, 13.29; Cl, 11.52. IR (KBr): 1626, 1377 cm^{-1}. AB in H_2O [λ_{max}, nm (ϵ, $mol^{-1}\ dm^3\ cm^{-1}$)]: 9.83×10^3 (10.48), 16.39×10^3 (8.26), 26.81×10^3 (13.91). Methanol and water were also useful as solvent for this reaction.

Method 2. A solution of $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ in aqueous ethanol was kept at room temperature with a stream of CO_2 for 40 min to give a blue precipitate of complex **2**, which was recrystallized from an ethanol–water solution (yield 82%).

Recovery of $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ (1) from Complex 2. N_2 gas was passed through an aqueous alcoholic solution containing complex **2** and excess amounts of *N,N*-Me_2en and $NaClO_4$ for 7 h at 60 °C. The resultant solution was filtered, and addition of diethyl ether to the solution gave a blue precipitate of the tris(diamine) complex **1** quantitatively. All manipulations were carried out under a nitrogen atmosphere.

Crystal Data and Intensity Measurements for $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4](ClO_4)_4$ (2). The crystal used in the data collection was a blue hexagonal column with the approximate dimensions 0.3 mm (width) × 0.5 mm (long). The crystal was mounted with the *c* axis approximately parallel to the instrument axis. Diffraction data were collected on a Rigaku AFC-4 four-circle automated diffractometer (controlled by a FACOM U-100 computer and the Rigaku FOS program system) equipped with Mo Kα radiation. Preliminary measurements showed the crystal system to be hexagonal with systematic absences ($00l$, $l = 2n + 1$) consistent with the space groups $P6_3$ and $P6_3/m$. Of the two possible space groups, the crystal structure was successfully refined in $P6_3$. The accurate unit cell dimensions were determined by the least-squares method with 20 reflections in the range of $20° < 2\theta < 30°$ on the diffractometer. The crystallographic and experimental data are summarized in Table I. Three standard reflection were monitored every 100 reflections and showed only a 2% random variation in intensity, for which no correction was made. The standard Lorentz, polarization, and absorption corrections were applied. For determination of the absolute configuration of the complex cation, intensities of 11 Bijvoet pairs (hkl, $hk\bar{l}$) were measured by the θ–2θ scan method with a scanning rate of 2 deg min^{-1}.

Table I. Crystallographic and Experimental Data for $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4](ClO_4)_4$ (**2**)

formula $Ni_3Cl_4O_{23}N_{12}C_{25}H_{80}$	fw 1237.8
cryst syst hexagonal	space group $P6_3$ (No. 173)
$a = 25.824$ (7) Å	$\lambda = 0.7107$ A (Mo Kα)
$c = 14.506$ (3) Å	$\rho_{obsd} = 1.49\ g\ cm^{-3}$, $\rho_{calcd} = 1.47\ g\ cm^{-3}$
$V = 8377$ (4) $Å^3$	$\mu = 12.8\ cm^{-1}$
$Z = 6$	$R^a = 0.065$
$T = 23$ °C	$R_w{}^b = 0.062$

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

Structure Solution and Refinement. The structure was solved by direct methods with MULTAN78.[19] The three nickel atoms were located in the initial *E* map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. These non-hydrogen atoms were refined anisotropically with the block-diagonal least-squares method to give $R = 0.080$ and $R_w = 0.079$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1$). At this stage, 11 reflections with large Bijvoet differences were selected and the absolute configuration of the complex cation was determined from the measurement of these reflections.[20,21] Accordance between the observed and calculated difference indicated that the absolute configuration is correct as that originally determined. Hydrogen atoms except for those of water molecules were placed by assuming a tetrahedral coordination about carbon and nitrogen atoms with C–H and N–H bond distances of 1.09 and 1.03 Å, respectively, and they were not refined. Finally, refinement converged with $R = 0.065$ and $R_w = 0.062$. Atomic scattering factors and values of f' and f'' for Ni, Cl, O, N, and C were taken from ref 22. A final difference Fourier synthesis showed peaks at heights up to 0.7 e A^{-3} around the chlorine atoms. In this structure refinement, perchlorate counteranions were significantly disordered except for one occupying a special position. Difference Fourier maps around the other three chlorine atoms led to an introduction of disordered models, six oxygen atoms with occupancy factors of $^2/_3$ being located around each chlorine atom. The final positional parameters along with their standard deviations for non-hydrogen atoms of the complex cation are listed in Table II. Compilations of observed and calculated structure factors are available as supplementary material. All calculations were performed on a FACOM M-780 computer at the Computer Center of the Institute of Physical and Chemical Research. Programs used were the UNICS III universal computing program[23] and MULTAN78[19] (direct methods).

Results and Discussion

Spontaneous Fixation of CO_2 in Air by $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$. When an aqueous ethanolic solution of $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ (**1**) was stirred in air and then its volume was reduced, blue crystals formulated as $Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4(ClO_4)_4$ (**2**) were obtained in a good yield. Complex **1** treated with 1 N H_2SO_4 released CO_2 gas and was also prepared by the reaction of $[Ni(N,N\text{-}Me_2en)_3](ClO_4)_2$ with a stream of carbon dioxide. Thus, complex **2** can be regarded as a product of spontaneous fixation of CO_2 in air by the nickel(II) complex of *N,N*-Me_2en. The fixation of CO_2 was also observed even in a water solution. The IR spectrum of **2** showed peaks at 1626 and 1377 cm^{-1} corresponding to $CO_3{}^{2-}$ (ν_3), which was not found in that of the starting complex. The frequency separation between the two components of ν_3 was comparable to those found in complexes with bidentate carbonate groups.[24] The visible and near-infrared spectrum of **2** in a H_2O solution consisted of three principal bands with comparatively low intensities, which are characteristic of octahedral nickel(II) complexes,[25] and the fre-

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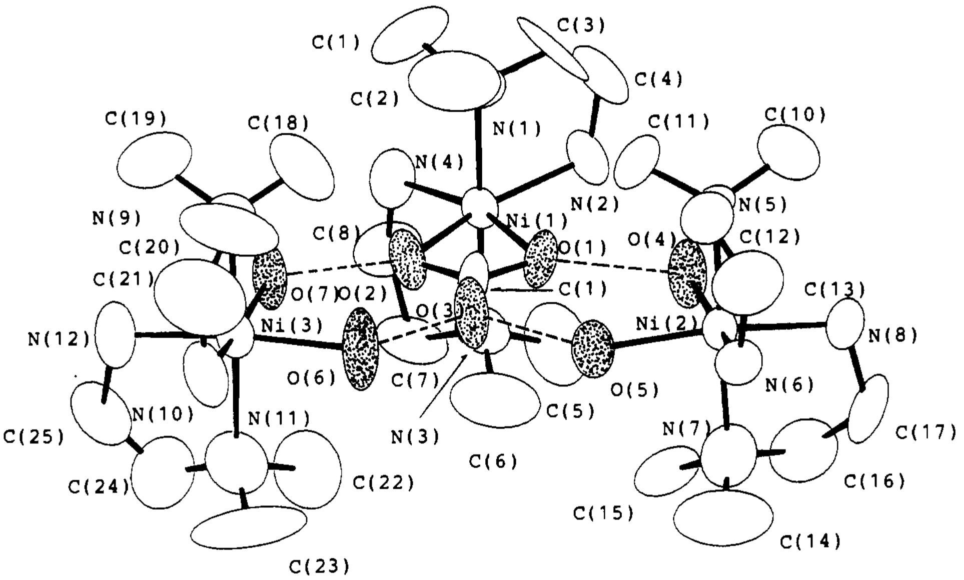
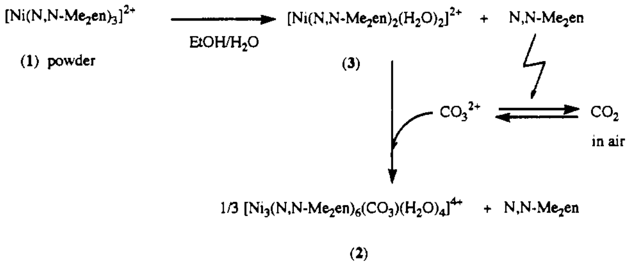


Figure 1. Perspective drawing of the complex cation of **2** with the numbering scheme for the atoms.

quencies of the first and second band maxima slightly shifted to the low energy side by 110–170 cm^{-1}, compared with those of *trans*-(*O*,*O*)-[Ni(*N*,*N*-Me_2en)$_2$(H_2O)$_2$]$^{2+}$ (**3**) in H_2O. These suggested that compound **2** has a [$Ni^{II}N_4O_2$] type structure. It was known that the tris(diamine) complex **1** dissolved in an aqueous medium dissociates into *trans*-(*O*,*O*)-[Ni(*N*,*N*-Me_2en)$_2$(H_2O)$_2$]$^{2+}$ (**3**) and *N*,*N*-Me_2en, because of the steric hindrance of *N*-methyl groups.[18] It was suggested that the bis(diamine) complex **3** is an active species in this fixation of CO_2. Further, an aqueous ethanolic solution of [Ni(*N*,*N*-Me_2en)$_2$(H_2O)$_2$](ClO_4)$_2$ did not show the similar uptake of CO_2 in air, indicating that the free *N*,*N*-Me_2en was indispensable to the present system. The free *N*,*N*-Me_2en was supposed to act as a base which raised the concentration of carbonate ions in the solution.[26] Complex **2** could be also prepared by the direct reaction of complex **1** with Na_2CO_3 in a yield of 84%. Thus, in the solution, CO_2 contamination in air was transformed into CO_3^{2-}, which was fixed on the metal center. When N_2 gas was passed through the solution of **2** in the presence of *N*,*N*-Me_2en and ClO_4^- for several hours at 60 °C, the starting complex **1** was recovered quantitatively.



When other salts of the complex **1** (Cl^-, Br^-, SO_4^{2-}, NO_3^-) were used as a starting material, only slight fixation of CO_2 in air was observed. The perchlorate salt of complex **1** is the most effective precursor for the spontaneous fixation of CO_2.

In order to clarify the detailed structure of **2**, an X-ray crystallographic study was undertaken.

Description of the Molecular Structure of [Ni_3(*N*,*N*-Me_2en)$_6$(CO_3)(H_2O)$_4$](ClO_4)$_4$ (2). A perspective drawing of the complex cation along with the numbering sheme for the atoms is given in Figure 1, and some selected interatomic distances and angles are presented in Table III. The trinuclear complex cation is made up of three octahedral nickel(II) complexes joined by an

Table II. Final Positional Parameters and B_{eq} Values for Non-Hydrogen Atoms of the Complex Cation of **2**[a,b]

atom	*x*	*y*	*z*	B_{eq}, Å$^{2\,c}$
Ni(1)	3825 (1)	4849 (1)	2081 (3)	3.2
Ni(2)	4519 (1)	2865 (1)	2074 (3)	3.4
Ni(3)	1265 (1)	2382 (1)	2147 (3)	3.6
O(1)	3887 (4)	4076 (4)	2020 (15)	4.1
O(2)	3020 (4)	4006 (4)	2009 (15)	4.7
O(3)	3082 (4)	3173 (4)	1959 (17)	5.7
O(4)	4674 (4)	3736 (4)	2124 (18)	5.6
O(5)	3602 (5)	2577 (5)	1978 (14)	4.9
O(6)	2013 (4)	2276 (5)	2095 (20)	6.9
O(7)	1860 (4)	3303 (5)	2238 (17)	5.8
N(1)	3812 (8)	4840 (7)	3579 (12)	5.2
N(2)	4735 (6)	5409 (6)	2347 (12)	4.5
N(3)	3865 (8)	4930 (8)	548 (12)	5.8
N(4)	3524 (7)	5463 (7)	1978 (19)	5.8
N(5)	4501 (6)	2875 (7)	3588 (9)	3.5
N(6)	4268 (7)	1958 (7)	2299 (12)	4.7
N(7)	4561 (9)	2847 (9)	545 (16)	7.3
N(8)	5449 (7)	3197 (7)	1953 (16)	5.5
N(9)	1227 (7)	2346 (7)	3632 (11)	4.4
N(10)	693 (7)	1436 (7)	2313 (18)	6.6
N(11)	1264 (10)	2377 (11)	599 (16)	8.7
N(12)	598 (6)	2601 (7)	1953 (18)	6.1
C(1)	3545 (18)	5220 (17)	3909 (22)	11.5
C(2)	3426 (16)	4245 (14)	4032 (18)	11.2
C(3)	4412 (11)	5138 (23)	3849 (16)	17.1
C(4)	4849 (10)	5474 (11)	3318 (19)	7.5
C(5)	4465 (12)	5259 (15)	174 (25)	11.2
C(6)	3704 (16)	4351 (13)	94 (22)	10.8
C(7)	3500 (18)	5128 (20)	257 (19)	12.8
C(8)	3558 (14)	5635 (12)	1003 (16)	7.6
C(9)	3323 (7)	3735 (7)	1969 (18)	3.8
C(10)	5091 (12)	3167 (16)	4035 (19)	10.0
C(11)	4106 (13)	3102 (16)	3904 (17)	9.2
C(12)	4173 (11)	2193 (12)	3876 (16)	6.5
C(13)	4297 (15)	1876 (13)	3320 (19)	8.7
C(14)	4299 (17)	2297 (12)	164 (21)	11.0
C(15)	4310 (13)	3189 (12)	93 (15)	7.1
C(16)	5193 (14)	3232 (15)	370 (18)	9.9
C(17)	5565 (12)	3140 (15)	968 (20)	9.0
C(18)	1796 (14)	2623 (16)	4049 (21)	10.4
C(19)	868 (16)	2628 (16)	4075 (22)	10.8
C(20)	968 (17)	1730 (16)	3879 (19)	13.0
C(21)	617 (17)	1331 (15)	3317 (22)	12.2
C(22)	1894 (13)	2826 (15)	230 (21)	10.4
C(23)	1109 (21)	1816 (13)	201 (19)	13.2
C(24)	860 (17)	2525 (22)	347 (21)	13.5
C(25)	518 (14)	2634 (17)	970 (18)	10.8

[a] Values are multiplied by 10^4. [b] Estimated standard deviations in parentheses. [c] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

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Table III. Selected Bond DIstances (Å) and Angles (deg)[a]

Bond Distances			
Ni(1)–O(1)	2.085 (13)	Ni(1)–O(2)	2.133 (8)
Ni(1)–N(1)	2.174 (17)	Ni(1)–N(2)	2.090 (13)
Ni(1)–N(3)	2.231 (18)	Ni(1)–N(4)	2.091 (21)
Ni(2)–O(4)	2.080 (12)	Ni(2)–O(5)	2.102 (12)
Ni(2)–N(5)	2.197 (14)	Ni(2)–N(6)	2.120 (18)
Ni(2)–N(7)	2.222 (23)	Ni(2)–N(8)	2.117 (16)
Ni(3)–O(6)	2.082 (14)	Ni(3)–O(7)	2.092 (10)
Ni(3)–N(9)	2.156 (16)	Ni(3)–N(10)	2.146 (15)
Ni(3)–N(11)	2.246 (23)	Ni(3)–N(12)	2.083 (21)
O(1)–C(9)	1.273 (16)	O(2)–C(9)	1.284 (25)
O(3)–C(9)	1.261 (19)		
Bond Angles			
O(1)–Ni(1)–O(2)	61.4 (5)	O(1)–Ni(1)–N(1)	92.3 (8)
O(1)–Ni(1)–N(2)	94.2 (6)	O(1)–Ni(1)–N(3)	91.4 (9)
O(1)–Ni(1)–N(4)	163.6 (6)	O(2)–Ni(1)–N(1)	92.1 (7)
O(2)–Ni(1)–N(2)	154.2 (6)	O(2)–Ni(1)–N(3)	91.3 (7)
O(2)–Ni(1)–N(4)	103.2 (5)	N(1)–Ni(1)–N(2)	80.1 (7)
N(1)–Ni(1)–N(3)	175.9 (7)	N(3)–Ni(1)–N(4)	82.8 (10)
O(4)–Ni(2)–O(5)	87.6 (5)	O(4)–Ni(2)–N(5)	86.9 (9)
O(4)–Ni(2)–N(6)	167.7 (8)	O(4)–Ni(2)–N(7)	94.2 (10)
O(4)–Ni(2)–N(8)	89.9 (6)	O(5)–Ni(2)–N(5)	92.5 (7)
O(5)–Ni(2)–N(6)	87.3 (6)	O(5)–Ni(2)–N(7)	89.2 (8)
O(5)–Ni(2)–N(8)	171.0 (8)	N(5)–Ni(2)–N(6)	82.2 (7)
N(5)–Ni(2)–N(7)	178.1 (9)	N(7)–Ni(2)–N(8)	82.4 (9)
O(6)–Ni(3)–O(7)	87.1 (5)	O(6)–Ni(3)–N(9)	93.2 (10)
O(6)–Ni(3)–N(10)	90.6 (6)	O(6)–Ni(3)–N(11)	87.8 (11)
O(6)–Ni(3)–N(12)	167.8 (9)	O(7)–Ni(3)–N(9)	88.8 (8)
O(7)–Ni(3)–N(10)	169.7 (10)	O(7)–Ni(3)–N(11)	93.9 (9)
O(7)–Ni(3)–N(12)	86.4 (6)	N(9)–Ni(3)–N(10)	81.3 (8)
N(9)–Ni(3)–N(11)	177.3 (6)	N(11)–Ni(3)–N(12)	82.4 (11)
Ni(1)–O(1)–C(9)	93.1 (12)	Ni(1)–O(2)–C(9)	90.6 (7)
O(1)–C(9)–O(2)	114.8 (14)	O(1)–C(9)–O(3)	122.1 (18)
O(2)–C(9)–O(3)	122.8 (13)		

[a] Estimated standard deviations in parentheses.

oxygen–hydrogen–oxygen bonding system. Each nickel atom is coordinated with four nitrogen atoms and two oxygen atoms which lie cis to one another. The absolute configuration of the complex cation determined by the Bijvoet method[21] is that Ni(1), Ni(2), and Ni(3) of the complex have the Λ, Λ, and Δ configuration, respectively. This indicated that a spontaneous optical resolution of the complex cations occurred during the recrystallization process. The Ni(1) atom is octahedrally coordinated with two bidentate diamines and a carbonate anion which acts as a bidentate ligand. Two oxygen atoms of the carbonate ligand lie cis, and two tertiary nitrogen atoms of the diamine ligands are in the trans position. Five-membered chelate rings, Ni(1)–N(1)–C(3)–C(4)–N(2) and Ni(1)–N(3)–C(7)–C(8)–N(4), adopt the flattened asymmetrical λ-gauche form. The coordination geometry around Ni(1) is significantly distorted from an octahedron owing to the bidentate carbonate ion, the smallest cis angle being 61.4° (O(1)–Ni(1)–O(2)) and the smallest trans angle 154.2° (O(2)–Ni(1)–N(2)). Such a small bit angle is common to those found for the same four-membered ring in other carbonate complexes.[10,12,27,28] The carbonate moiety is essentially planar, and the four-membered ring formation around Ni(1) causes the carbonate O(1)–C(9)–O(2) bond angle to decrease from 120 to 114.8 (14)°. As concerns the C–O bond distances, they are almost equal (C(9)–O(1) = 1.27 (2), C(9)–O(2) = 1.28 (3), C(9)–O(3) = 1.26 (2) Å) unlike those in the bidentate carbonate systems,[27] presumably attributable to the hydrogen bonding network described later. The Ni(2) and Ni(3) atoms are also octahedrally coordinated with two bidentate diamines and two water molecules, in which two oxygen atoms of the coordinating water molecules lie cis and two tertiary nitrogen atoms of the diamines are trans like the Ni(1) unit. As far as we know, structurally characterized cis-(*O*,*O*)-[Ni(diamine)$_2$(H$_2$O)$_2$]$^{2+}$ complexes are very rare, and the isolation of such a compound could be attributable to the hydrogen bonding network around the carbonate ion. The absolute configurations around Ni(2) and Ni(3) are Λ and Δ, respectively; that is, two nickel complexes that are nearly enantiomeric with respect to each other. The coordination geometries of both complexes are slightly distorted octahedral with the smallest cis angles of 82.2 (7)° (N(5)–Ni(2)–N(6)) and 81.3 (8)° (N(9)–Ni(3)–N(10)) and the smallest trans angles of 167.7 (8)° (O(4)–Ni(2)–N(6)) and 167.8 (9)° (O(6)–Ni(3)–N(12)). Two diamine chelate rings around the Ni(2) atom, Ni(2)–N(5)–C(12)–C(13)–N(6) and Ni(2)–N(7)–C(16)–C(17)–N(8), adopt the asymmetrical λ-gauche form, and two around the Ni(3) atom, Ni(3)–N(9)–C(20)–C(21)–N(10) and Ni(3)–N(11)–C(24)–C(25)–N(12), take the flattened δ-gauche form and envelope form, respectively. The three octahedral nickel complex units are joined by a novel hydrogen bonding system between the carbonate ligand and the coordinating water molecules (Figure 2). The distances of O(1)···O(4) = 2.59 (2), O(2)···O(5) = 2.50 (2), O(3)···O(6) = 2.57 (1), and O(2)···O(7) = 2.64 (1) Å fall within the range for O···H–O hydrogen bondings,[28] although hydrogen atoms in this system were not located in the present X-ray analysis despite some attempt to do so. This hydrogen bonding network including carbonate ligand is spread in the plane defined by the three nickel atoms. Furthermore, the six nitrogen atoms of the primary amino groups are included in the plane with a maximum deviation of 0.42 (2) Å (N(2)) (Table IV). In other words, the trinuclear cation has a wide spread equatorial plane around the carbonate ligand. The oxygen atoms of perchlorate anions are not involved in this hydrogen bonding network. From this structure, it is presumed that the bidentate carbonate ligand is stabilized by the other two nickel complexes of the diamine ligand, *cis*-(*O*,*O*)-[Ni(*N*,*N*-Me$_2$en)$_2$(H$_2$O)$_2$]$^{2+}$, via the planar hydrogen bonding system, resulting in that the coordinating carbonate ligand strongly resists disconnection from the metal center even in vacuo. Con-

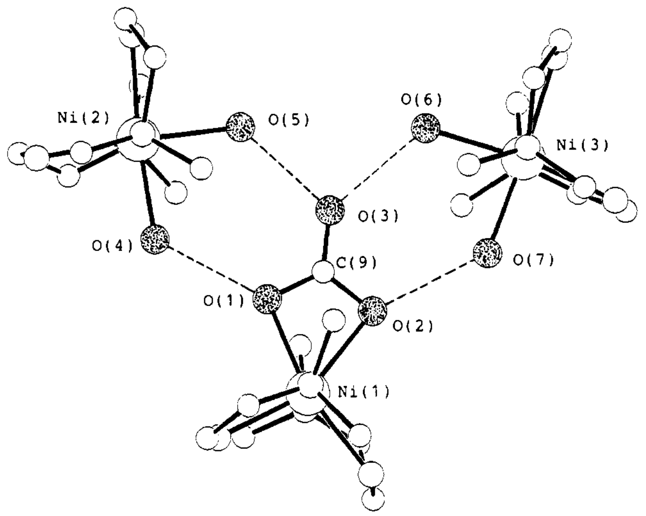

Figure 2. Perspective view of the complex cation of **2** projected vertical to the equatorial plane.

Table IV. Deviations of Atoms (Å) from the Plane Defined by Three Nickel Atoms (Ni(1)–(Ni(3))[a]

Ni(1)	0.0	Ni(2)	0.0
Ni(3)	0.0	O(1)	0.09 (2)
O(2)	0.14 (2)	O(3)	0.21 (2)
O(4)	–0.08 (3)	O(5)	0.17 (2)
O(6)	0.05 (3)	O(7)	–0.16 (2)
N(2)	–0.42 (2)	N(4)	0.16 (3)
N(6)	–0.31 (2)	N(8)	0.14 (2)
N(10)	–0.22 (3)	N(12)	0.30 (3)
C(9)	0.19 (3)		

[a] Estimated standard deviations in parentheses.

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sequently, this novel hydrogen bonding system could be regarded as a significant driving force to the spontaneous fixation of CO_2 under atmospheric conditions.

As to the solution-phase structure of complex **2**, whether the hydrogen bonding system was retained or not was not yet clear.

Examinations with Other *N*-Alkyl-Substituted Diamines. Analogous diamines were examined to elucidate the N-substituent effect on the CO_2 uptake. When *N*-methylethylenediamine, *N*-ethylethylenediamine, and *N*,*N*-diethylethylenediamine were used as the diamine part, no fixation of CO_2 in air was observed. *N*-Methylethylenediamine and *N*-ethylethylenediamine were likely to form tris(diamine)nickel(II) complexes, and *N*,*N*-diethylethylenediamine led to precipitation of a bis(diamine) square-planar nickel(II) complex. Further, *N*,*N'*-dimethylethylenediamine (*N*,*N'*-Me_2en), which forms preferably *trans*-(*O*,*O*)-$[Ni(N,N'\text{-}Me_2en)_2(H_2O)_2]^{2+}$ in an aqueous medium, failed to adsorb CO_2 in air. This is probably due to the instability of the *cis*-(*O*,*O*)-$[Ni(N,N'\text{-}Me_2en)_2(H_2O)_2]^{2+}$ unit. Thus, the N-substituents of ethylenediamine dramatically influenced the present system, and the spontaneous fixation of CO_2 is unique to the nickel(II)–*N*,*N*-Me_2en system.

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Supplementary Material Available: Listings of crystallographic data, positional and anisotropic thermal parameters, atomic parameters of hydrogen atoms, and bond distances and bond angles and a figure showing crystal packing (12 pages); a table of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Spectroscopic Properties of a Novel Mixed-Valence Compound Containing Tetrabromocuprate(II) and Tribromocuprate(I) Anions

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The preparation, crystal structure, electronic and ESR spectra are reported for the mixed valence Cu(II)/Cu(I) compound $[LH_3]_4[CuBr_3][CuBr_4]\cdot H_2O\cdot 3CH_3OH$ (where LH_2 = 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil). The compound crystallizes in the triclinic space group $P1$ with $a = 15.069$ (5), $b = 16.207$ (7), $c = 16.519$ (5) Å, $\alpha = 90.50$ (3), $\beta = 107.67$ (3), $\gamma = 105.40$ (3)°, $Z = 2$, $R = 0.089$, and $R_w = 0.068$. The $[CuBr_4]^{2-}$ anion shows a distorted tetrahedral geometry with bond lengths in the range 2.340 (4)–2.396 (3) Å and angles of two types, 125.7 (2)–133.0 (2)° and 98.4 (1)–101.8 (1)°. The $[CuBr_3]^{2-}$ anion has a planar triangular geometry with very approximate C_{2v} symmetry. The bond lengths and angles are in the ranges 2.347 (4)–2.398 (4) Å and 117.4 (2)–123.9 (1)°, respectively. Intermolecular distances between the ions and solvent molecules suggest extensive hydrogen bonding network.

Introduction

6-Amino-1,3-dimethyl-5((2-carboxyphenyl)azo)uracil (hereafter denoted as LH_2) can coordinate to metal ions as a bidentate, a tridentate, and a tetradentate ligand, yielding mononuclear, dinuclear and tetranuclear metal complexes, respectively, which present interesting magnetic properties.[1-3] We have recently reported a tetranuclear compound $[Cu_4(L)_3(LH)(NO_3)(H_2O)]\cdot 2H_2O$ having a quasi-tetrahedral arrangement of the four copper(II) atoms and a ferromagnetic ground state.[3] In an attempt to prepare new tetranuclear complexes of this type, a compound having the formula $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ was obtained. The present paper is devoted to the structural and spectroscopic studies of this compound, which have revealed that $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ is a mixed-valence Cu(II)/Cu(I) compound containing $[CuBr_4]^{2-}$ and $[CuBr_3]^{2-}$ anions. Compounds having a metal in two valence states are of special interest because of the possibility of electron transfer between these states, which is of great importance in a large range of chemical and biochemical catalytic systems.[4] Cu(II)/Cu(I) compounds present an additional interest, because of different coordination numbers and stereochemistry adopted by Cu(II) and Cu(I); both oxidation states are labile and stereochemically flexible. From these reasons, the chemistry of mixed-valence Cu(II)/Cu(I) compounds has received considerable attention in the last few years. Thus, a number of these compounds has been prepared and their structures determined by X-ray diffraction methods.[5]

Table I. Crystallographic Data for $[LH_3]_4[CuBr_3][CuBr_4]\cdot H_2O\cdot 3CH_3OH$

chem formula: $C_{55}H_{68}Cu_2Br_7N_{20}O_{20}$	chem formula: $C_{55}H_{68}Cu_2Br_7N_{20}O_{20}$
$a = 15.069$ (5) Å	fw = 2015.70
$b = 16.207$ (7) Å	space group: $P1$ (No. 2)
$c = 15.519$ (5) Å	T = 23–25 °C
$\alpha = 90.50$ (3)°	$\lambda = 0.71069$
$\beta = 107.67$ (3)°	$\rho_{calcd} = 1.82$ g cm^{-3}
$\gamma = 105.40$ (3)°	$R = 0.089$
$V = 3688$ (2) Å^3	$R_w{}^a = 0.069$
$Z = 2$	

[a] The function minimized with $R_w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$.

Experimental Section

Synthesis. LH_2 was synthesized by coupling diazotized anthranilic acid with 6-amino-1,3-dimethyluracil, according to the method described by Lythgoe et al.[6] The compound was recrystallized from hot pyridine

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