Table III. Magnetic Properties of Selected Dimers, $[Cu(O_2CR)_2L]_2$[a]

R	L	α[b]	$-2J$, cm^{-1}	ref
H	NCS^-	0.42	485	9
CF_3	quinoline	2.07	310	10
CH_3	H_2O	2.19	284	11
CCl_3	2-Cl-py	7.77	217	6
CBr_3	2-Cl-py	10.95	180	this work

[a] The dimers chosen for this table were those for a given R for which the best combination of crystallographic and magnetic data are available. Inclusion of dimers with other addends L, where available, would not alter the ordering shown. [b] The tabulated values are group polarizabilities, evaluated from the atomic polarizabilities given in: Ketelaar, J. A. A. "Chemical Constitution"; Elsevier: Amsterdam, 1958; p 91.

fluence on the magnetic behavior of copper(II) carboxylate dimers than does the nature of the addend L. This provides further support for the validity of comparing $2J$ values for dimers with different axial ligands.

The principal result of this study is that the three dimers with R = CBr_3 have, by a significant margin, the smallest interaction (i.e., the least negative $2J$ values) of the series of dimers with R = H, methyl, or trihalomethyl. Data for a representative set of such dimers are tabulated in Table III. From these data it is evident that the ordering of $2J$ values is identical with the ordering of group polarizabilities of the substituents R. By providing an extreme point on the polarizability scale, the data for the tribromoacetate adducts significantly strengthen the observed relationship. Although this empirical correlation works remarkably well for one particular series of closely related groups, it does not appear to extend to other, more complicated, substituents. Thus, for example, dimeric adducts of the higher copper(II) alkanoates have $2J$ values of comparable, or slightly greater, magnitude than the acetate adducts.[12] In view of recent theoretical results, which describe the coupling in these dimers as the resultant of several different modes of interaction,[13] it is not surprising that meaningful correlations of $2J$ with ligand properties are found only for sets of dimers in which the bridging carboxylate ligands are closely related.

At this time, the apparent relationship between $2J$ and ligand polarizability for this series of dimers must be regarded as strictly an empirical one, whose fundamental significance (if any) is not clear. However, because of the scarcity of good structure/magnetism correlations for these dimers, it may well be of use as a calibration point for future theoretical efforts. It is certainly more reasonable that $2J$ should be related to a free-ligand property like polarizability than to an aqueous solution property such as the pK_a of the parent acid, which has been the basis for some earlier proposed correlations, including one for the haloacetates.[1]

Acknowledgment. We are grateful to Professor Christopher Reed and Dr. Peter Boyd for their help with the magnetic measurements. The purchase of the SQUID magnetometer at the University of Southern California was made possible by a grant from the National Science Foundation.

Registry No. $[Cu(O_2CCBr_3)_2L]_2$ (L = 2-chloropyridine), 88801-76-7; $[Cu(O_2CCBr_3)_2L]_2$ (L = 2-methylpyridine), 88801-75-6; $[Cu(O_2CCBr_3)_2L]$ (L = quinoline), 88801-77-8.

Supplementary Material Available: Tables of experimental parameters, observed and calculated structure factors, anisotropic thermal parameters, positional parameters of hydrogen atoms, bond distances, bond angles, and magnetic susceptibility data (18 pages). Ordering information is given on any current masthead page.

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Solution and Solid-State ^{113}Cd NMR of $Cd(\alpha,\alpha'\text{-bpy})_2X_2$ ($X = Cl^-, Br^-, NCS^-, NO_3^-, H_2O$) and Crystal Structures of the Nitrate (Monohydrate) and the Isothiocyanate Derivatives

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The crystal structures of bis(α,α'-bipyridyl)cadmium(II) nitrate hemihydrate (A) and bis(isothiocyanato)bis(bipyridyl)-cadmium(II) (B) have been determined. The structure of A consists of two crystallographically and chemically different Cd^{2+} species separated from each other by ordinary van der Waals distances. Each Cd is approximately octahedrally coordinated, with four N and two O donor ligands. However, the coordinated oxygens for Cd(1) are from a nitrate oxygen and a water of hydration oxygen while for Cd(2) both oxygen atoms are from nitrate oxygen atoms. The CP/MAS solid-state ^{113}Cd NMR of A consists of two resonances at +51 and +123 ppm deshielded from the usual $Cd(ClO_4)_2$ standard. The D_2O solution of this compound is a single resonance at +172, uniquely identifying all three signals as corresponding to water of hydration of 0, 1, and 2, respectively, bound to Cd. The crystal structure of B consists of approximately octahedral Cd^{2+}, with six N donors separated by ordinary van der Waals distances. The CP/MAS ^{113}Cd NMR signal of B is at +216 ppm. The analogous chloride and bromide salts have CP/MAS ^{113}Cd NMR signals +250 and +185 ppm. A: $a = 14.372$ (1) Å, $b = 35.134$ (2) Å, $c = 17.174$ (4) Å, $D_x = 1.74$ g/cm^3, $D_M = 1.93$ g/cm^3, $Z = 16$, *Pcab*, $\mu = 10.63$ cm^{-1}, maximum-minimum transmittance factor = 0.887-0.430, NO = 3636, NV = 604, $R_F = 0.066$. B: $a = 16.274$ (6) Å, $b = 16.75$ (1) Å, $c = 16.136$ (7) Å, $D_x = 1.63$ g/cm^3, $D_M = 1.62$ (2) g/cm^3, $Z = 8$, *Pcab*, $\mu = 11.93$ cm^{-1}, maximum-minimum transmittance factor = 0.899-0.876, NO = 2331, NV = 280, $R_F = 0.032$.

Introduction

^{113}Cd NMR has recently shown itself to be a useful tool as a probe of the geometric and electronic environment of the Cd nucleus in a wide variety of compounds ranging from inorganic species through organometallics to biological macromolecules.[1-42] The potential of ^{113}Cd NMR has been further

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Table I. Cell Data, Data Collection, and Refinement Parameters for Bis(bipyridyl)cadmium(II) Nitrate Hemihydrate (A) and Bis(bipyridyl)bis(isothiocyanato)cadmium(II) (B)

diffractometer: Enraf-Nonius CAD-4
λ(Mo Kα) = 0.710 73 Å
A: a = 14.372 (1) Å, b = 35.134 (2) Å, c = 17.174 (4) Å, D_x = 1.74 g/cm^3, D_{measd} = 1.93 g/cm^3, Z = 16, fw = 566.8, $C_{20}N_6O_{7.5}N_{21}Cd$
B: a = 16.274 (6) Å, b = 16.75 (1) Å, c = 16.136 (9) Å, D_x = 1.63 g/cm^3, D_{measd} = 1.62 (2) g/cm^3, Z = 8, fw = 540.9, $C_{22}H_{16}N_6S_2Cd$, space group *Pcab*
systematic absences for A and B: $h0l$, $h = 2n + 1$; $0kl$, $l = 2n + 1$; $hk0$, $k = 2n + 1$
faces: (A) {100}, {010}, {001}; (B) {100}, {010}, {101}, {$\bar{1}$01}
max/min transmission factors and abs cor: (A) 0.887/0.430, μ = 10.63 cm^{-1};[50] (B) 0.899/0.876, μ = 11.93 cm^{-1} [50]
cryst size: (A) ~0.58 × 0.53 × 0.56 mm; (B) ~0.10 × 0.09 × 0.29 mm
P factor = 0.030 in $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (PI_{\text{raw}})^2]^{1/2}/Lp$ and $w = 1/\sigma(F_o^2)$
data considered nonzero if (A) $F^2 > 3\sigma(F^2)$ (NO = 3636) and (B) $F^2 > 4\sigma(F^2)$ (NO = 2331)
12 083 (A) and 6385 (B) reflcns measd in θ–2θ mode to 2θ = 70 and 60°, respectively
unobsd reflcns: (A) 997, $>F_{\text{min}}$ = 29.0; (B) 565, $>F_{\text{min}}$ = 17.3
variable scan speed with preliminary scan speed of 4°/min in 2θ
25 general reflcns used in orientation matrix (checked every 24 h) and used for parameter measurements
3 std reflcns monitored every 100 reflcns; decay less than 2% I
room temp ~18 °C
structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous dispersion corrections with weights based upon intensity statistics[48] function minimized here and below $\Sigma_i w_i[|F_o|_i - |F_c|]_i^2$
final least squares performed on Amdahl V6[51] with f, $\Delta f'$, and $\Delta f''$ from ref 52
largest shift at end of refinement: (A) 0.17σ; (B) 0.07σ
av shift: (A) 0.04σ; (B) 0.01σ
no. of variables: (A) 604; (B) 280
final R: (A) 0.066; (B) 0.032
weighted R: (A) 0.064; (B) 0.032
error in obsn of unit wt: (A) 2.25; (B) 1.40; $F(000)$: (A) 4464; (B) 2160
final difference Fourier qualitatively featureless
hydrogen atoms located and included in structure factor calculations for B but not further refined
no attempt made to find hydrogen atoms in A

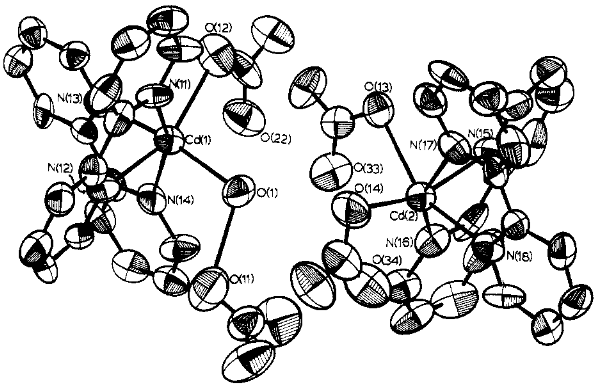

Figure 1. An ORTEP drawing of the isolated molecules of (α,α'-bipyridyl)$_2$(H_2O)Cd(NO_3)$_2$ and (α,α'-bpy)$_2$Cd(NO_3)$_2$ (A). Cd(1) is bound to O(1) (H_2O), which in turn is hydrogen bonded to an oxygen (O(11)) of a nitrate group. Cd(2) is bound to two oxygens of nitrate groups, O(13) and O(14). The ellipsoids are drawn at 50% probability level. For clarity not all the atom numbering is shown. However, for purposes of the reading of the tables they are as follows: O(12), O(22), N(32), O(32); O(11), N(21), O(21), O(31); O(14), N(44), O(24), O(34); O(13), N(43), O(23), O(33) are the groups that make up the nitrate ions. N(11) is bound to C(11) and the numbers proceed to C(51) bound to N(11) in a counterclockwise fashion. C(51) is bound to C(12) which is bound to N(12) and C(22); the numbering proceeds counterclockwise to C(52) bound to N(12). N(13) is bound to C(13) counterclockwise to C(53) bound to N(13), and C(14) is bound to N(14) counterclockwise to C(54) bound to N(14). N(17) is bound to C(17) counterclockwise to ···C(57). C(17) is bound to C(58) bound to N(18) then counterclockwise to C(18)···C(58). N(15) is bound to C(15) clockwise to ···C(55) bound to N(15) and C(55); C(55) is bound to C(16) bound to N(16) and C(16) clockwise to ···C(56) bound to N(16).

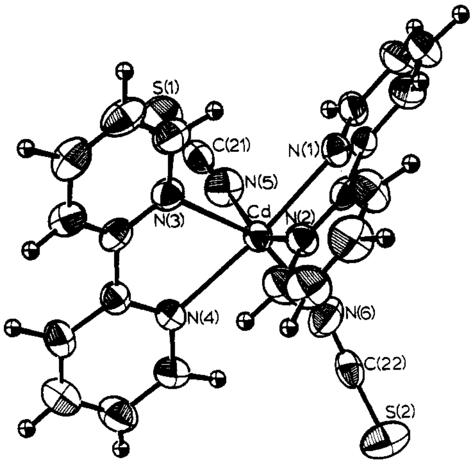

Figure 2. An ORTEP drawing of the isolated molecule of B. The ellipsoids are drawn as for A. For clarity not all atom designations are shown. However, for purposes of the reading of the tables the unlabeled atoms are as follows: C(11) is bound to N(3) and the numbering is sequential in a counterclockwise manner to C(15) also bound to N(3). C(16) is joined to C(15) and N(4) and the numbering proceeds counterclockwise to N(4). C(1) is bound to N(1) and the numbering proceeds clockwise to C(5) bound to N(1) and C(6), which is also bound to N(2); the numbering proceeds clockwise to C(10) bound to N(2).

enhanced by the development of cross-polarization and magic-angle-spinning (CP, MAS) observations of the ^{113}Cd NMR in the solid state.[15,43-49] One of the limiting factors in the application of this NMR probe has been the lack of X-ray

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{equiv}[a]	atom	x	y	z	B_{equiv}[a]
(A) Bis(α,α-bipyridyl)cadmium(II) Nitrate Hemihydrate									
Cd(1)	0.28939 (6)	0.40048 (2)	0.29684 (5)	3.56	C(33)	0.0451 (9)	−0.0468 (4)	0.389 (1)	5.28
Cd(2)	0.29607 (6)	−0.36285 (2)	0.46171 (5)	3.53	C(43)	0.0874 (9)	−0.0823 (4)	0.403 (1)	5.79
O(1)	0.4032 (6)	0.3652 (2)	0.3500 (6)	5.48	C(53)	0.1532 (8)	0.4046 (4)	0.1521 (7)	3.06
N(11)	0.2584 (8)	0.4345 (3)	0.4111 (6)	3.79	C(14)	0.2015 (9)	−0.1336 (4)	0.3591 (8)	3.82
N(12)	0.1701 (7)	0.3696 (3)	0.3700 (8)	4.67	C(24)	0.1821 (9)	0.3431 (4)	0.0778 (8)	4.08
N(13)	0.1759 (7)	0.4256 (3)	0.2143 (6)	3.75	C(34)	0.233 (1)	0.3077 (4)	0.0718 (8)	4.90
N(14)	0.2630 (7)	−0.1428 (3)	0.3041 (7)	4.36	C(44)	0.298 (1)	−0.2017 (4)	0.3689 (9)	5.02
N(15)	0.3305 (7)	−0.3917 (3)	0.0345 (8)	4.28	C(54)	0.310 (1)	−0.1775 (4)	0.3073 (8)	5.45
N(16)	0.2294 (8)	−0.3291 (3)	0.0772 (6)	4.44	O(23)	0.0206 (7)	−0.4379 (3)	0.0788 (6)	6.56
N(17)	0.2427 (8)	−0.3993 (3)	0.3511 (6)	4.14	N(43)	0.0689 (8)	−0.4139 (3)	0.0445 (8)	4.22
N(18)	0.1863 (7)	0.1719 (3)	0.1079 (6)	3.85	O(34)	0.3932 (9)	−0.3034 (3)	0.4187 (7)	8.12
O(12)	0.3762 (7)	0.4582 (3)	0.2670 (7)	6.83	O(24)	0.4924 (8)	−0.3064 (4)	0.3258 (7)	8.53
O(13)	0.1366 (7)	0.0767 (3)	0.4971 (5)	4.88	N(44)	0.439 (1)	−0.3223 (5)	0.3718 (8)	5.66
O(14)	0.4222 (7)	−0.3572 (3)	0.3707 (7)	7.86	C(15)	0.374 (1)	0.0765 (4)	0.4838 (9)	5.20
O(33)	0.0565 (7)	0.1205 (3)	0.4478 (6)	6.26	C(25)	0.436 (1)	0.0558 (4)	0.433 (1)	5.99
O(11)	0.3452 (8)	−0.2013 (3)	0.1016 (8)	8.54	C(35)	0.450 (1)	0.0721 (5)	0.362 (1)	7.13
O(21)	0.4076 (9)	0.2493 (3)	0.4483 (8)	10.19	C(45)	0.411 (1)	−0.3939 (5)	0.160 (1)	6.57
O(31)	0.463 (1)	−0.2266 (4)	0.1538 (8)	11.38	C(55)	0.350 (1)	−0.3761 (4)	0.107 (1)	4.58
O(22)	0.4250 (7)	0.4124 (3)	0.1941 (7)	7.57	C(16)	0.300 (1)	0.1597 (4)	0.3770 (8)	4.69
N(21)	0.408 (1)	0.2743 (4)	0.3973 (9)	5.98	C(26)	0.324 (1)	−0.3181 (5)	0.1908 (9)	6.67
O(32)	−0.0207 (8)	0.0306 (3)	0.1775 (7)	7.38	C(36)	0.273 (1)	0.2156 (5)	0.294 (1)	6.99
N(32)	0.4272 (9)	0.4465 (4)	0.2128 (8)	5.34	C(46)	0.197 (1)	0.2256 (4)	0.342 (1)	6.20
C(11)	0.304 (1)	−0.0327 (4)	0.0747 (7)	4.75	C(56)	0.176 (1)	−0.2977 (4)	0.0904 (9)	5.39
C(21)	0.221 (1)	0.4889 (4)	−0.007 (1)	5.52	C(18)	0.159 (1)	0.2066 (4)	0.0867 (8)	4.67
C(31)	0.288 (1)	−0.0249 (4)	0.4542 (9)	5.88	C(28)	0.0892 (9)	0.2279 (4)	0.1239 (8)	4.55
C(41)	0.3333 (9)	0.4399 (4)	0.0261 (9)	5.20	C(38)	0.0426 (9)	−0.2905 (4)	0.3166 (9)	4.82
C(51)	0.194 (1)	0.4208 (4)	0.4585 (8)	4.27	C(48)	0.0660 (8)	0.1732 (4)	0.2109 (8)	4.70
C(12)	0.1491 (9)	−0.1161 (4)	0.0630 (9)	3.84	C(58)	0.1423 (9)	0.1549 (4)	0.1676 (9)	4.49
C(22)	0.4127 (9)	−0.1338 (4)	0.5078 (9)	5.22	C(17)	0.1759 (8)	0.1169 (8)	0.1932 (8)	3.53
C(32)	0.046 (1)	−0.1679 (5)	0.029 (1)	6.15	C(27)	0.148 (1)	0.0981 (4)	0.2642 (9)	5.60
C(42)	0.065 (1)	0.3172 (4)	0.396 (1)	5.46	C(37)	0.191 (1)	−0.4362 (4)	0.214 (1)	5.84
C(52)	0.1282 (9)	0.3366 (4)	0.3491 (9)	5.18	C(47)	0.256 (1)	−0.4520 (4)	0.262 (1)	5.01
C(13)	0.1347 (9)	0.4591 (4)	0.2261 (8)	4.05	C(57)	0.284 (1)	−0.4330 (4)	0.3310 (9)	5.15
C(23)	0.0666 (9)	−0.0254 (4)	0.3231 (9)	4.33					
(B) Bis(bipyridyl)cadmium(II) Isothiocyanate									
Cd	0.68113 (1)	0.49918 (2)	0.11110 (1)	2.69 (2)	C(8)	0.9337 (4)	0.4675 (4)	−0.0784 (4)	5.6 (3)
S(1)	0.49185 (9)	0.66685 (9)	0.28144 (9)	5.24 (7)	C(9)	0.9203 (4)	0.4131 (4)	−0.0169 (4)	5.5 (3)
S(2)	0.58269 (9)	0.25311 (8)	−0.0195 (1)	5.59 (7)	C(10)	0.8530 (4)	0.4234 (3)	0.0338 (4)	4.7 (3)
N(1)	0.6840 (2)	0.5974 (2)	0.0050 (2)	2.9 (1)	C(11)	0.8350 (3)	0.6118 (3)	0.1784 (3)	4.2 (3)
N(2)	0.7977 (2)	0.4815 (2)	0.0223 (3)	3.1 (2)	C(12)	0.9068 (3)	0.6317 (3)	0.2203 (4)	4.8 (3)
N(3)	0.7911 (2)	0.5459 (3)	0.1972 (3)	3.4 (2)	C(13)	0.9346 (3)	0.5818 (4)	0.2821 (4)	4.7 (3)
N(4)	0.7092 (2)	0.4069 (2)	0.2204 (2)	2.9 (2)	C(14)	0.8887 (3)	0.5141 (3)	0.3022 (3)	3.7 (3)
N(5)	0.5852 (3)	0.5691 (3)	0.1790 (3)	4.2 (2)	C(15)	0.8175 (2)	0.4980 (4)	0.2591 (3)	3.0 (3)
N(6)	0.6075 (3)	0.4037 (3)	0.0458 (3)	5.1 (3)	C(16)	0.7680 (3)	0.4262 (3)	0.2757 (3)	3.0 (2)
C(1)	0.6248 (3)	0.6514 (3)	−0.0027 (3)	3.2 (2)	C(17)	0.7809 (3)	0.3795 (3)	0.3462 (3)	4.0 (2)
C(2)	0.6247 (3)	0.7097 (3)	−0.0631 (3)	4.0 (3)	C(18)	0.7312 (4)	0.3136 (3)	0.3602 (3)	4.8 (3)
C(3)	0.6924 (3)	0.7124 (3)	−0.1159 (3)	4.4 (3)	C(19)	0.6707 (3)	0.2942 (3)	0.3038 (4)	4.6 (3)
C(4)	0.7535 (3)	0.6566 (3)	−0.1093 (3)	3.8 (2)	C(20)	0.6622 (3)	0.3417 (3)	0.2339 (3)	3.8 (3)
C(5)	0.7467 (3)	0.5992 (2)	−0.0484 (3)	2.7 (2)	C(21)	0.5464 (3)	0.6111 (3)	0.2213 (3)	3.3 (2)
C(6)	0.8096 (3)	0.5344 (3)	−0.0383 (3)	2.9 (2)	C(22)	0.5980 (3)	0.3400 (3)	0.0198 (3)	3.4 (2)
C(7)	0.8771 (4)	0.5291 (3)	−0.0900 (3)	4.7 (3)					

[a] $B_{\text{equiv}} = 8\pi^2\,{}^1/_3\,\Sigma_i\Sigma_j U_{ij} a_i{}^* a_j{}^* \overline{a}_i \cdot \overline{a}_j$.

structural data and the corresponding ^{113}Cd (CP, MAS) solid-state NMR data as well as the appropriate solution data.

We desired to examine a system in which the stereochemistry would be well-defined and invariant to substitution of the

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Table III. Bonded Distances (Å) and Angles (deg) with Esd's in Parentheses

(A) Bis(α,α′-bipyridyl)cadmium(II) Nitrate Hemihydrate

Cd(1)-O(1)	2.246 (9)	C(11)-C(21)	1.44 (2)	C(15)-C(25)	1.46 (2)
Cd(1)-O(12)	2.43 (1)	C(21)-C(31)	1.41 (2)	C(25)-C(35)	1.36 (3)
Cd(1)-N(11)	2.35 (1)	C(31)-C(41)	1.43 (2)	C(35)-C(45)	1.37 (3)
Cd(1)-N(12)	2.39 (1)	C(41)-C(51)	1.40 (2)	C(45)-C(55)	1.40 (2)
Cd(1)-N(13)	2.34 (1)	C(51)-N(11)	1.32 (2)	C(55)-N(15)	1.40 (2)
Cd(1)-N(14)	2.34 (1)	N(12)-C(12)	1.30 (2)	N(16)-C(16)	1.34 (2)
Cd(2)-O(13)	2.435 (9)	C(12)-C(22)	1.44 (2)	C(16)-C(26)	1.45 (2)
Cd(2)-O(14)	2.41 (1)	C(22)-C(32)	1.39 (2)	C(26)-C(36)	1.41 (3)
Cd(2)-N(15)	2.43 (1)	C(32)-C(42)	1.39 (3)	C(36)-C(46)	1.42 (3)
Cd(2)-N(16)	2.35 (1)	C(42)-C(52)	1.41 (2)	C(46)-C(56)	1.46 (2)
Cd(2)-N(17)	2.42 (1)	C(52)-N(12)	1.36 (2)	C(56)-N(16)	1.36 (2)
Cd(2)-N(18)	2.33 (1)	N(13)-C(13)	1.33 (2)	N(17)-C(17)	1.35 (2)
O(1)-O(11)	2.61 (1)	C(13)-C(23)	1.40 (2)	C(17)-C(27)	1.45 (2)
O(11)-N(21)	1.24 (2)	C(23)-C(33)	1.40 (2)	C(27)-C(37)	1.40 (2)
N(21)-O(21)	1.24 (2)	C(33)-C(43)	1.41 (2)	C(37)-C(47)	1.37 (2)
N(21)-O(31)	1.19 (2)	C(43)-C(53)	1.42 (2)	C(47)-C(57)	1.42 (2)
O(12)-N(32)	1.26 (2)	C(53)-N(13)	1.34 (2)	C(57)-N(17)	1.37 (2)
N(32)-O(22)	1.24 (2)	N(14)-C(14)	1.34 (2)	N(18)-C(18)	1.33 (2)
N(32)-O(32)	1.26 (2)	C(14)-C(24)	1.39 (2)	C(18)-C(28)	1.40 (2)
O(13)-N(43)	1.25 (2)	C(24)-C(34)	1.45 (2)	C(28)-C(38)	1.38 (2)
N(43)-O(23)	1.24 (2)	C(34)-C(44)	1.42 (2)	C(38)-C(48)	1.40 (2)
N(43)-O(33)	1.23 (2)	C(44)-C(54)	1.37 (2)	C(48)-C(58)	1.47 (2)
O(14)-N(44)	1.25 (2)	C(54)-N(14)	1.39 (2)	C(58)-N(18)	1.35 (2)
N(44)-O(24)	1.23 (2)	C(12)-C(51)	1.49 (2)	C(16)-C(55)	1.48 (2)
N(44)-O(34)	1.24 (2)	C(14)-C(53)	1.52 (2)	C(17)-C(58)	1.48 (2)
N(11)-C(11)	1.35 (2)	N(15)-C(15)	1.31 (2)		

O(1)-Cd(1)-O(12)	100.0 (3)	O(22)-N(32)-O(32)	120 (1)	N(14)-C(14)-C(53)	115 (1)
O(1)-Cd(1)-N(11)	94.3 (4)	O(12)-N(32)-O(32)	120 (1)	C(14)-C(24)-C(34)	117 (1)
O(1)-Cd(1)-N(12)	93.2 (3)	Cd(2)-O(13)-N(43)	104.3 (7)	C(24)-C(34)-C(44)	119 (1)
O(1)-Cd(1)-N(13)	164.6 (4)	O(13)-N(43)-O(23)	121 (1)	C(34)-C(44)-C(54)	120 (1)
O(1)-Cd(1)-N(14)	93.7 (3)	O(13)-N(43)-O(33)	116 (1)	C(44)-C(54)-N(14)	121 (1)
O(12)-Cd(1)-N(11)	81.5 (4)	O(23)-N(43)-O(33)	122 (1)	C(55)-N(15)-C(15)	117 (1)
O(12)-Cd(1)-N(12)	148.9 (4)	Cd(2)-O(14)-N(44)	102.7 (9)	N(15)-C(15)-C(25)	125 (1)
O(12)-Cd(1)-N(13)	85.1 (4)	O(14)-N(44)-O(24)	124 (1)	C(15)-C(25)-C(35)	115 (1)
O(12)-Cd(1)-N(14)	117.7 (4)	O(14)-N(44)-O(34)	115 (1)	C(25)-C(35)-C(45)	123 (2)
N(11)-Cd(1)-N(12)	69.5 (4)	O(24)-N(44)-O(34)	121 (2)	C(35)-C(45)-C(55)	118 (2)
N(11)-Cd(1)-N(13)	100.9 (4)	C(51)-N(11)-C(11)	122 (1)	C(45)-C(55)-N(15)	122 (1)
N(11)-Cd(1)-N(14)	157.5 (4)	N(11)-C(11)-C(21)	119 (1)	C(45)-C(55)-C(16)	124 (1)
N(12)-Cd(1)-N(13)	89.6 (4)	C(11)-C(21)-C(31)	121 (1)	N(15)-C(55)-C(16)	114 (1)
N(12)-Cd(1)-N(14)	89.1 (4)	C(21)-C(31)-C(41)	117 (1)	C(56)-N(16)-C(16)	124 (1)
N(13)-Cd(1)-N(14)	71.2 (4)	C(31)-C(41)-C(51)	119 (1)	N(16)-C(16)-C(26)	120 (1)
O(13)-Cd(2)-O(14)	87.9 (3)	C(41)-C(51)-N(11)	122 (1)	C(26)-C(16)-C(55)	119 (1)
O(13)-Cd(2)-N(15)	77.5 (3)	C(41)-C(51)-C(12)	120 (1)	N(16)-C(16)-C(55)	121 (1)
O(13)-Cd(2)-N(16)	104.6 (4)	N(11)-C(51)-C(12)	118 (1)	C(16)-C(26)-C(36)	118 (1)
O(13)-Cd(2)-N(17)	84.0 (4)	C(52)-N(12)-C(12)	118 (1)	C(26)-C(36)-C(46)	120 (1)
O(13)-Cd(2)-N(18)	151.1 (4)	N(12)-C(12)-C(22)	124 (1)	C(36)-C(46)-C(56)	119 (1)
O(14)-Cd(2)-N(15)	159.3 (4)	C(22)-C(12)-C(51)	118 (1)	C(46)-C(56)-N(16)	118 (1)
O(14)-Cd(2)-N(16)	129.0 (4)	N(12)-C(12)-C(51)	117 (1)	C(17)-N(17)-C(57)	122 (1)
O(14)-Cd(2)-N(17)	76.5 (4)	C(12)-C(22)-C(32)	117 (1)	N(17)-C(17)-C(27)	119 (1)
O(14)-Cd(2)-N(18)	97.4 (4)	C(22)-C(32)-C(42)	119 (1)	C(27)-C(17)-C(58)	125 (1)
N(15)-Cd(2)-N(16)	69.8 (4)	C(32)-C(42)-C(52)	119 (1)	N(17)-C(17)-C(58)	116 (1)
N(15)-Cd(2)-N(17)	87.2 (4)	C(42)-C(52)-N(12)	122 (1)	C(17)-C(27)-C(37)	120 (1)
N(15)-Cd(2)-N(18)	88.8 (4)	C(53)-N(13)-C(13)	120 (1)	C(27)-C(37)-C(47)	119 (1)
N(16)-Cd(2)-N(17)	152.5 (4)	N(13)-C(13)-C(23)	124 (1)	C(37)-C(47)-C(57)	121 (1)
N(16)-Cd(2)-N(18)	94.0 (4)	C(13)-C(23)-C(33)	116 (1)	C(47)-C(57)-N(17)	119 (1)
N(17)-Cd(2)-N(18)	69.8 (4)	C(23)-C(33)-C(43)	122 (1)	C(58)-N(18)-C(18)	118 (1)
Cd(1)-O(1)-O(11)	113.0 (4)	C(33)-C(43)-C(53)	117 (1)	N(18)-C(18)-C(28)	125 (1)
O(1)-O(11)-N(21)	112 (1)	C(43)-C(53)-N(13)	122 (1)	C(18)-C(28)-C(38)	116 (1)
O(21)-N(21)-O(11)	118 (1)	C(43)-C(53)-C(14)	120 (1)	C(28)-C(38)-C(48)	124 (1)
O(21)-N(21)-O(31)	121 (1)	N(13)-C(53)-C(14)	118 (1)	C(38)-C(48)-C(58)	114 (1)
O(11)-N(21)-O(31)	121 (2)	C(54)-N(14)-C(14)	120 (1)	C(48)-C(58)-N(18)	123 (1)
Cd(1)-O(12)-N(32)	100.5 (9)	N(14)-C(14)-C(24)	123 (1)	C(48)-C(58)-C(17)	119 (1)
O(22)-N(32)-O(12)	120 (1)	C(24)-C(14)-C(53)	122 (1)	N(18)-C(58)-C(17)	118 (1)

(B) Bis(bipyridyl)cadmium(II) Isothiocyanate

Cd-N(1)	2.374 (4)	C(3)-C(4)	1.369 (8)	C(10)-N(2)	1.337 (7)	C(16)-C(17)	1.396 (7)
Cd-N(2)	2.398 (4)	C(4)-C(5)	1.379 (7)	N(3)-C(11)	1.349 (7)	C(17)-C(18)	1.387 (8)
Cd-N(3)	2.396 (4)	C(5)-N(1)	1.336 (6)	C(11)-C(12)	1.391 (8)	C(18)-C(19)	1.379 (8)
Cd-N(4)	2.388 (4)	C(5)-C(6)	1.501 (7)	C(12)-C(13)	1.376 (9)	C(19)-C(20)	1.387 (7)
Cd-N(5)	2.239 (4)	N(2)-C(6)	1.333 (6)	C(13)-C(14)	1.397 (8)	C(20)-N(4)	1.351 (6)
Cd-N(6)	2.260 (5)	C(6)-C(7)	1.384 (8)	C(14)-C(15)	1.377 (7)	N(5)-C(21)	1.167 (6)
N(1)-C(1)	1.329 (6)	C(7)-C(8)	1.396 (9)	C(15)-N(3)	1.350 (7)	C(21)-S(1)	1.615 (5)
C(1)-C(2)	1.378 (7)	C(8)-C(9)	1.364 (9)	C(15)-C(16)	1.474 (7)	N(6)-C(22)	1.157 (7)
C(2)-C(3)	1.395 (8)	C(9)-C(10)	1.379 (9)	N(4)-C(16)	1.347 (6)	C(22)-S(2)	1.607 (6)

N(1)-Cd-N(2)	68.8 (1)	Cd-N(1)-C(1)	121.6 (3)	C(5)-C(6)-C(7)	121.6 (4)	Cd-N(4)-C(16)	117.9 (3)
N(1)-Cd-N(3)	100.1 (1)	Cd-N(1)-C(5)	119.8 (3)	C(6)-C(7)-C(8)	119.4 (5)	Cd-N(4)-C(20)	122.3 (3)
N(1)-Cd-N(4)	167.5 (1)	C(1)-N(1)-C(5)	118.6 (4)	C(7)-C(8)-C(9)	119.0 (6)	C(16)-N(4)-C(20)	119.3 (4)

Table III (*Continued*)

N(1)-Cd-N(5)	90.3 (1)	N(1)-C(1)-C(2)	123.2 (5)	C(8)-C(9)-C(10)	118.4 (6)	N(4)-C(16)-C(15)	117.7 (4)
N(1)-Cd-N(6)	99.6 (1)	C(1)-C(2)-C(3)	117.1 (5)	C(9)-C(10)-N(2)	122.9 (5)	N(4)-C(16)-C(17)	120.7 (4)
N(2)-Cd-N(3)	78.2 (1)	C(2)-C(3)-C(4)	120.3 (5)	Cd-N(3)-C(11)	122.2 (3)	C(15)-C(16)-C(17)	121.6 (4)
N(2)-Cd-N(4)	102.2 (1)	C(3)-C(4)-C(5)	118.2 (5)	Cd-N(3)-C(15)	118.1 (3)	C(16)-C(17)-C(18)	119.4 (5)
N(2)-Cd-N(5)	155.5 (2)	C(4)-C(5)-N(1)	122.5 (4)	C(11)-N(3)-C(15)	118.9 (4)	C(17)-C(18)-C(19)	119.8 (5)
N(2)-Cd-N(6)	93.0 (1)	C(4)-C(5)-C(6)	121.7 (4)	N(3)-C(11)-C(12)	122.1 (5)	C(18)-C(19)-C(20)	118.1 (5)
N(3)-Cd-N(4)	69.0 (1)	N(1)-C(5)-C(6)	115.8 (4)	C(11)-C(12)-C(13)	118.8 (5)	C(19)-C(20)-N(4)	122.6 (5)
N(3)-Cd-N(5)	93.8 (1)	Cd-N(2)-C(6)	118.1 (3)	C(12)-C(13)-C(14)	119.0 (5)	Cd-N(5)-C(21)	168.6 (4)
N(3)-Cd-N(6)	153.8 (2)	Cd-N(2)-C(10)	122.7 (3)	C(13)-C(14)-C(15)	119.5 (5)	N(5)-C(21)-S(1)	178.3 (6)
N(4)-Cd-N(5)	96.3 (1)	C(6)-N(2)-C(10)	119.1 (4)	C(14)-C(15)-N(3)	121.6 (5)	Cd-N(6)-C(22)	153.3 (4)
N(4)-Cd-N(6)	89.2 (1)	C(5)-C(6)-N(2)	117.4 (4)	C(14)-C(15)-C(16)	121.9 (4)	N(6)-C(22)-S(2)	177.7 (6)
N(5)-Cd-N(6)	103.2 (2)	N(2)-C(6)-C(7)	121.1 (4)	N(3)-C(15)-C(16)	116.5 (4)		

anionic sites such as CdL_4X_2 in which L_4 would remain unchanged by the substitution of anion X by anion Y. One such system is where L_4 are the nitrogen atoms from two bipyridyl ligands. We present here the structural details of two members of this series as well as the solid-state (CP, MAS) and solution ^{113}Cd NMR results.

Experimental Section

Bis(α,α'-bipyridyl)cadmium(II) nitrate was prepared in situ by dissolving 1.56 g (0.01 mol) of α,α'-bipyridyl (Fisher) and 1.54 g (0.005 mol) of $Cd(NO_3)_2{\cdot}4H_2O$ (Baker and Adamson) in 200 mL of H_2O.

The resulting solution was warmed gently (~80 °C) for 1 h and 0.01 mol of the appropriate salt (NaCl, NaBr, NaI, NaSCN) dissolved in 50 mL of water was added with stirring. The metathesis reaction was essentially instantaneous in all instances and the resultant precipitates were collected, washed, and air-dried. Except for the isothiocyanate product, all were insoluble in common solvents and could not be crystallized. The isothiocyanate was sparingly soluble in hot dimethylformamide, and small diffraction quality crystals were obtained from this medium.

X-ray Data. The data collection techniques and structure solution and refinement details are summarized in Table I. The structure factor tables have been deposited along with the anisotropic thermal parameters and the hydrogen parameters. The atomic positional and equivalent isotropic temperature factors for A and B are found in Table II. Table III contains the bonded distances and angles. ORTEP[53] drawings of A and B are found in Figures 1 and 2. A packing diagram of A has been deposited.

NMR Data. The ^{113}Cd NMR methanol or DMF solution data were collected on a highly modified XL-100-15 spectrometer described earlier or on a Bruker WP200 spectrometer. Natural abundance ^{113}Cd was used throughout. The solution spectra were measured over a concentration range of 35 mM to 105 mM. A small concentration dependence of ~3 ppm was observed. A typical peak width at half-peak height was found to be 20 Hz. The external standard was 0.1 M aqueous $Cd(ClO_4)_2$ solution (see Table IV).

Solid-state ^{113}Cd NMR spectra were obtained from ca. 0.5-g samples containing the natural abundance ^{113}Cd nuclide on a modified Bruker WP200 (USC) or on a Nicolet NT-200 (CSU) spectrometer at 44.42 MHz (4.7 T) using cross-polarization (CP) and magic-angle-spinning (MAS) techniques. The contact time was 4 ms, the ^1H-90° spin-locking time was 5 ms, and the recycle time was 4 s. Rotor speeds of approximately 4 kHz were employed. A "solid solution" (finely dispersed mixture) of "concentration" 0.1 M $Cd(H_2O)_6^{2+}$-$(ClO_4)_2$ in Al_2O_3 was used as an external standard (see Table IV).

Description of Structures and Discussion

The structure of A, bis(bipyridyl)cadmium(II) nitrate hemihydrate, is most readily described as two crystallographically and chemically independent, approximately octahedrally coordinated Cd^{2+}, ions. Each of these ions may be described as CdN_4O_2 coordination polyhedra but $Cd^{2+}(1)$ contains an oxygen [O(1)] from a water molecule at one of the coordination sites and a nitrate oxygen [O(12)] at the other, whereas for $Cd^{2+}(2)$ both oxygen atoms [O(13), O(14)] in the coordination sphere are from nitrate oxygen atoms. The water oxygen [O(1)] in the coordination sphere of $Cd^{2+}(1)$ is in turn hydrogen bonded to the remaining nitrate group of $Cd^{2+}(1)$ via a hydrogen bond with O(11). Thus, we have two chemically distinct species separated from each other and from neighboring molecules by ordinary van der Waals distances. It is to be noted that the Cd–O(1) (water) distance of 2.246 (9) Å is considerably shorter than the Cd–O(nitrate) distances to O(12), O(13), and O(14) of 2.43 (1), 2.435 (9), and 2.41 (1) Å respectively, which together with the Cd(1)–O(1)–O(11) angle of 113.0 (4)° implies that a lone pair of electrons from the water oxygen is essentially pointed toward the Cd atom. These observations are particularly relevant to the ^{113}Cd chemical shift, vide infra. As expected the N–Cd–N angles within the chelate ring are less than 90°, ranging from 69.5 (4) to 71.2 (4)° with no obvious reason for this difference, and we attribute it to intermolecular or interligand contacts. The N–Cd–N nonchelating angles of adjacent nitrogens are 100.9 (4), 89.1 (4), 87.2 (4), and 94.0 (4)°, larger than the internal angles, but not routinely greater than 90°. It is interesting to note that the O(1)–Cd–X angles are all greater than 90°. These features may be understood if one examines the Cd(1)–O(22), Cd(2)–O(33), and Cd(2)–O(34) distances of 2.67 (1), 2.62 (1), and 2.69 (1) Å, i.e., there seems to be some weak interaction with a second oxygen of each nitrate group tending to push back the bipyridyl ligands. Whether this is due to some real chemical bonding or to simply orientational demands of the nitrate group is not clear.

The structure of B, bis(isothiocyanato)bis(bipyridyl)cadmium(II) can be easily understood as simply replacement of the nitrate or water oxygen atoms of A by the isothiocyanate donor. Hence, we have a CdN_6 moiety with only van der Waals distances between molecules (Figure 2). In this case, in contrast to A, the Cd–N(bipyridyl) distances are very regular at 2.389 Å, average, and all four distances are within four standard deviations. The Cd–N(isothiocyanate) distances are 2.239 (4) and 2.260 (4) Å and are expected to be shorter than the above. As above, the interior N–Cd–N angles are ~69° and the exterior N–Cd–N angles are ~100°. Perhaps the most surprising feature of this structure is the N(5)–Cd–N(6) (isothiocyanate N–Cd–isothiocyanate N) angle of 103.2 (2)°. Another interesting feature is that of formation of the isothiocyanate rather than the thiocyanate since Cd generally prefers S coordination to nitrogen coordination.

Discussion of Structures and ^{113}Cd NMR

The ^{113}Cd resonance of A in D_2O solution consists of a single line at +172 ppm (deshielded from the standard) and the solid state CP/MAS ^{113}Cd resonance consists of two signals at +123 and +51 ppm, Table IV. In D_2O solution A must be a $CdN_4(OD_2)_2$ coordination polyhedron and the approximately

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Table IV. ^{113}Cd NMR of Cd(bpy)$_2$X$_2$ Species (0 ppm[a] = 0.1 M Cd(ClO$_4$)$_2$ in D$_2$O)

compd	solution	CP/MAS solid (Hw, ppm)[b]
1. Cd(bpy)$_2$-(NO$_3$)$_2$·$^1/_2$H$_2$O	+66 (4) (DMF)[c] +172 (5) (D$_2$O)	+123 (13), 51 (12)
2. Cd(bpy)$_2$Cl$_2$	*d*	+250 (46)
3. Cd(bpy)$_2$Br$_2$	*d*	+185 (28)
4. Cd(bpy)$_2$I$_2$	*d*	*d*
5. Cd(bpy)$_2$(NCS)$_2$	+122 (5) (Me$_2$SO)[c]	+216 (24)

[a] Positive values represent greater deshielding than the standard. [b] Hw = half-width of resonance at half peak height. [c] Concentration range 1. = 56–125 mM with 4 ppm variation 5. = 77–118 mM with 5 ppm variation. [d] No ^{113}Cd NMR signal observed, due to solubility problems or simply not observable in solid state experiments.

50 ppm shift from the +123 ppm signal is due to the second water molecule in the coordination polyhedron replacing the oxygen of nitrate in the NO$_3$H$_2$OCdN$_4$ONO$_2$ coordination of the crystallographic Cd(1). The second signal in the CP/MAAs ^{113}Cd NMR at +51 ppm is then due to the CdN$_4$O$_2$ [Cd(2)] bound to the pyridyl nitrogen and the oxygen of the nitrate groups. This is also consistent with our observations[54] that oxygen atoms of nitrate groups coordinated to Cd tend to make the ^{113}Cd nucleus more shielded. It is also in line with our postulate that poorer electron donors (certainly nitrate oxygen is one) will shield the ^{113}Cd nucleus relative to better donors. This is, in this case, nitrate oxygen compared to water oxygen.

The relative positions of the ^{113}Cd NMR isotropic chemical shifts in Table IV can be understood in these same terms. The model we propose in order to understand the isotropic ^{113}Cd chemical shift is the following. The most shielded ^{113}Cd nucleus is the gaseous bare Cd^{2+} ion with an electronic configuration Kr(4d)^{10}(5s)^0. Any chemical bonding will involve mixing of these orbitals with ligand orbitals, whether it be d or inner shell sp, and will only deshield the ^{113}Cd nucleus. Therefore, it is not unreasonable to view the chemical shifts in Table IV in terms of a CdN$_4$X$_2$ octahedron; the best classical chemical bond (Cd–X) is that of N$_4$Cd–Cl$_2$, followed by N$_4$Cd–(NCS)$_2$, N$_4$Cd–Br$_2$, N$_4$Cd–(OH$_2$)$_2$, N$_4$Cd(OH$_2$)-(ONO$_2$), and N$_4$Cd–(ONO$_2$) with chemical shifts of +250, +216, +185, +172, +123, and +51 ppm, respectively.

It is unfortunate that the ^{113}Cd NMR of the Cd(bpy)$_2$I$_2$ was not observed either in solution or in the solid state. We do not believe the Cd(bpy)(NCS)$_2$ ^{113}Cd NMR spectrum observed in Me$_2$SO is meaningful relative to the above model because of the solution properties of Me$_2$SO. It is interesting to note from a ^{113}Cd NMR utilization point of view that the unexpected isocyanate structure is clearly established by the ^{113}Cd NMR CP/MAS solid-state results.

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Registry No. A, 81521-32-6; B, 88801-78-9; Cd(bpy)$_2$Br$_2$, 77130-38-2; Cd(bpy)$_2$I$_2$, 56270-76-9; Cd(bpy)$_2$Cl$_2$, 77139-24-3; Cd(bpy)$_2$(OH$_2$)$_2$, 88801-79-0; ^{113}Cd, 14336-66-4.

Supplementary Material Available: Listings of anisotropic temperature factors, hydrogen atom coordinates and distances, angles involving hydrogen atoms, and observed and calculated structure factors and a packing figure of A (48 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Imidazolate-Bridged Dicopper(II) Ion in Two Binucleating Macrocycles

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The synthesis and structural characterization of complexes containing the imidazolate-bridged dicopper(II) core bound within two different binucleating macrocyclic ligands are reported. The ligands used in this study were 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (macrocycle A) and 1,4,7,13,16,19-hexaazacyclotetracosane (macrocycle A′). Imidazolate-bridged dicopper complexes form readily upon addition of 1 equiv of imidazole (imH) and 1 equiv of sodium hydroxide to an aqueous solution of the ligand and 2 equiv of copper(II) perchlorate. Crystals suitable for X-ray diffraction experiments were best obtained upon addition of a fifth ligand (L = imH or 1-methylimidazole (MeIm)) to give pentacoordinate copper atoms. Insertion of the [Cu$_2$(im)L$_2$]$^{3+}$ unit into the macrocyclic ligand cavity results in distorted trigonal bipyramidal geometries for the two copper centers, with Cu–N bond lengths ranging from 1.95 to 2.26 Å. The complex [Cu$_2$(im)(imH)$_2$$\subset$A](ClO$_4$)$_3$ crystallizes in the monoclinic system, space group *C2/c*, with a = 15.008 (3) Å, b = 10.186 (2) Å, c = 26.062 (3) Å, β = 100.48 (1)°, and Z = 4. For [Cu$_2$(im)(1-MeIm)$_2$$\subset$A′](ClO$_4$)$_3$, X-ray studies revealed orthorhombic symmetry, space group *Pnma*, with a = 16.670 (4) Å, b = 28.112 (18) Å, c = 9.195 (9) Å and Z = 4.

Introduction

The metalloenzyme bovine erythrocyte superoxide dismutase (BESOD) has been the subject of extensive research.[2,3] Its structure has been determined by X-ray crystallography.[4] Each of the two identical subunits contains an imidazolate- (histidine-) bridged bimetallic active site incorporating one

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