Notes

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Crystal and Molecular Structure of Dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II), an Example of an Oxygen-Bonded Arylnitroso Ligand

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Received March 15, 1989

4-Nitroso-*N*,*N*-dimethylaniline is used as a test for the presence of transition metals in water. Solutions containing only the free ligand are green whereas solutions containing the complexed ligand are usually purple. There are several modes of binding of the RN═O ligands to transition metals that have either been observed or proposed. Oxygen-binding metal complexes of arylnitroso ligands are to date a rare occurrence. Dichlorobis(nitrosobenzene)palladium(II) is square planar and the RN═O ligands are nitrogen bonded.[3] Dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)cobalt(II) is tetrahedral, and it was reported by Sams and Doedens that the RN═O ligands were also nitrogen bonded.[4] The only reported example of an oxygen-bound arylnitroso ligand is in dichlorodimethylbis(4-nitroso-*N*,*N*-dimethylaniline)tin(IV),[5] which is octahedral.

Attempts have been made to develop criteria by which oxygen and nitrogen bonding of RN═O ligands might be differentiated by I.R. spectroscopy.[4,5] This study of the zinc(II) complex was undertaken to investigate the basis of the color change, the coordination geometry of the zinc atom, the binding mode of the arylnitroso ligand, and criteria for the differentiation between oxygen and nitrogen bonding of RN═O ligands from IR spectroscopic data.

Experimental Section

Startng Materials. 4-Nitroso-*N*,*N*-dimethylaniline for the IR studies was prepared by using the procedure of ref 6 followed by washing the crystal with cold diethyl ether. All reagents and solvents used were commercially available and subjected to simple drying or distillation as appropriate.

Preparation of the Complex. A solution of $ZnCl_2$ (11.0 mmol) in ethanol (50 mL) was mixed with the ligand (22.1 mmol) in ethanol (50 mL) and heated on a hot plate. The crimson crystals separated after the solution was heated and reduced to a small volume. The materials was then stirred several times in ether and dried in vacuo over $CaCl_2$. The procedure yielded dark red crystals of $ZnCl_2[(CH_3)_2NC_6H_4NO]_2$.

For the X-ray work 4-nitroso-*N*,*N*-dimethylaniline was obtained from Aldrich Chemical Co., Inc., and was purified by recrystallization from anhydrous ether. Dichlorodimethylbis(4-nitroso-*N*,*N*-dimethylaniline)tin(IV) for the IR studies was obtained by using the procedure of ref 5.

Collection and Reduction of X-ray Data. The crystal chosen for data collection had 10 faces and had approximate dimensions 0.32 × 0.16 × 0.31 mm and a measured density (flotation) of 1.54 g cm^{-3}. Crystal data are summarized in Table I.

Data collection was carried out on a modified Picker FACSI diffractometer controlled by the NRCC diffractometer system[7] using graphite-monochromated Mo Kα radiation. Lattice parameters were also determined at 295 K by using 104 reflections ($5° \leq 2\theta \leq 48°$). The $\theta/2\theta$ scan mode was used to collect 3306 independent reflections, $0 \leq h \leq 16$, $0 \leq k \leq 34$, and $0 \leq l \leq 10$ ($3° \leq 2\theta \leq 50°$), of which 2236 ($I > 2\sigma(I)$) were used in the refinement.

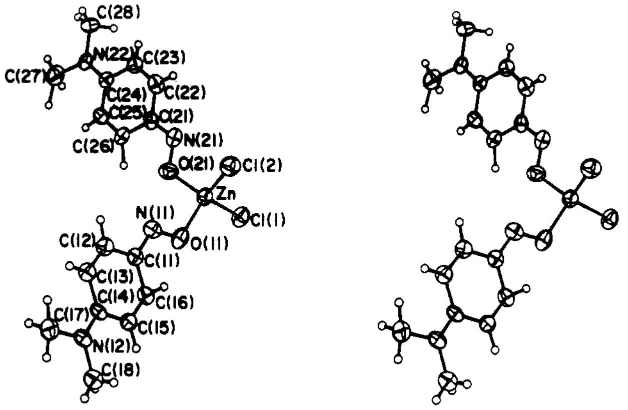

Figure 1. ORTEP drawing of the molecular structure with the atomic numbering system for dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II). Hydrogen atom labeling has been omitted for clarity.

Table I. Crystallographic Data for Dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II)

$ZnCl_2[(CH_3)_2NC_6H_4NO]_2$	M_r = 436.65
a = 14.263 (6) Å	space group: *Pbca*
b = 28.848 (8) Å	T = 295 K
c = 9.156 (3) Å	λ = 0.71069 Å
V = 3767 (3) Å^3	ρ_{obs} = 1.54 (1) g cm^{-3}
Z = 8	ρ_{calc} = 1.539 g cm^{-3}
$R(F_o)$ = 0.049	μ = 16.4 cm^{-1}
$R_w(F_o)$ = 0.028	transm coeff = 0.641–0.774

Structure Solution and Refinement. Lorentz and polarization and absorption corrections, using the Gaussian method, were applied. The structure was solved by direct methods. Full-matrix least-squares refinement with the non-hydrogen atoms anisotropic and hydrogen atoms isotropic, using the X-RAY 76 programs,[8] gave an R value of 0.050 and an R_w value of 0.060 using the 2236 independent reflections with $I > 2\sigma(I)$ and weights calculated as $\sigma(F)^{-2}$, where $\sigma(F)$ is based on counting statistics and instrument instability. Further refinement (with modified weights[9,10] using XTAL[11] gave R = 0.049 and R_w = 0.028. Anomalous scattering factors for Zn and Cl were taken from ref 12. Atomic parameters are given in Table II and bond distances and angles are given in Table III.

Collection of IR Data. All infrared spectral data were collected by using KBr disks and a Perkin-Elmer FT-IR 1600 Series spectrophotometer.

Results and Discussion

An ORTEP diagram of the molecular structure of dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II) and its numerical labeling are shown in Figure 1.

IR spectral data for the free ligand, the title compound, the Sn complex, which has octahedral coordination, and $PdCl_2[(CH_3)_2NC_6H_4NO]_2$,[16] which has square-planar coordination, are given in Table IV. Binding of the arylnitroso ligands with the

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0020-1669/89/1328-4552$01.50/0

Table II. Positional Parameters and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms

atom	*x*	*y*	*z*	U_{equiv}, Å^2
Zn	0.17930 (3)	0.11534 (1)	0.46888 (4)	3.34 (2)
Cl(1)	0.28242 (7)	0.08828 (4)	0.3069 (1)	4.84 (6)
O(11)	0.1109 (2)	0.06066 (9)	0.5507 (3)	4.1 (2)
N(11)	0.0381 (2)	0.0736 (1)	0.6269 (3)	3.9 (2)
C(11)	−0.0044 (3)	0.0394 (1)	0.7017 (4)	3.2 (2)
C(12)	−0.0810 (3)	0.0523 (2)	0.7890 (4)	3.6 (3)
C(13)	−0.1254 (3)	0.0225 (1)	0.8789 (4)	3.7 (3)
C(14)	−0.0936 (2)	−0.0244 (1)	0.8890 (4)	3.0 (2)
C(15)	−0.0185 (3)	−0.0387 (1)	0.7948 (4)	3.5 (3)
C(16)	−0.0246 (3)	−0.0077 (1)	0.7053 (4)	3.7 (3)
N(12)	−0.1320 (2)	−0.0540 (1)	0.9840 (3)	3.4 (2)
C(17)	−0.1017 (5)	−0.1020 (2)	0.9941 (6)	4.8 (4)
C(18)	−0.2113 (3)	−0.0413 (2)	1.0743 (2)	4.7 (3)
Cl(2)	0.23825 (8)	0.15409 (3)	0.6592 (1)	4.87 (7)
O(21)	0.0812 (2)	0.14865 (9)	0.3552 (3)	4.2 (2)
N(21)	0.0981 (2)	0.1928 (1)	0.3383 (3)	3.8 (2)
C(21)	0.0354 (2)	0.2153 (1)	0.2556 (4)	3.4 (2)
C(22)	−0.0429 (3)	0.1951 (2)	0.1821 (4)	3.6 (3)
C(23)	−0.1038 (3)	0.2214 (1)	0.1050 (5)	3.6 (3)
C(24)	−0.0900 (2)	0.2705 (1)	0.0924 (4)	3.2 (2)
C(25)	−0.0105 (3)	0.2905 (2)	0.1641 (4)	3.8 (3)
C(26)	0.0486 (3)	0.2636 (4)	0.2402 (4)	4.1 (3)
N(22)	−0.1496 (2)	0.2969 (1)	0.0173 (3)	3.3 (2)
C(27)	−0.2348 (3)	0.2777 (2)	−0.0477 (7)	5.3 (3)
C(28)	−0.1376 (4)	0.3468 (2)	0.048 (5)	4.3 (3)

Table III. Bond Lengths (A) and Angles (deg)

Zn–Cl(1)	2.230 (1)	Zn–Cl(2)	2.234 (1)
Zn–O(1)	2.001 (2)	Zn–O(21)	1.991 (2)
O(11)–N(11)	1.305 (4)	O(21)–N(21)	1.304 (4)
N(11)–C(11)	1.345 (4)	N(21)–C(21)	1.339 (4)
C(11)–C(12)	1.403 (4)	C(21)–C(22)	1.429 (5)
C(12)–C(13)	1.350 (5)	C(22)–C(23)	1.353 (5)
C(13)–C(14)	1.427 (5)	C(23)–C(24)	1.433 (5)
C(14)–C(15)	1.435 (4)	C(24)–C(25)	1.432 (5)
C(15)–C(16)	1.350 (5)	C(25)–C(26)	1.342 (5)
C(16)–C(11)	1.421 (5)	C(26)–C(21)	1.413 (5)
C(14)–N(12)	1.337 (4)	C(24)–N(22)	1.333 (5)
N(12)–C(17)	1.454 (5)	N(22)–C(27)	1.462 (4)
N(12)–C(18)	1.447 (4)	N(22)–C(28)	1.453 (5)
Cl(1)–Zn–O(21)	106.54 (8)	Cl(2)–Zn–O(11)	106.63 (8)
Cl(1)–Zn–Cl(2)	116.47 (5)	O(11)–Zn–O(21)	103.51 (9)
Cl(1)–Zn–O(11)	107.14 (7)	Cl(2)–Zn–O(21)	115.50 (7)
Zn–O(11)–N(11)	111.3 (2)	Zn–O(21)–N(21)	113.8 (2)
O(11)–N(11)–C(11)	114.9 (3)	O(21)–N(21)–C(21)	114.6 (3)
N(11)–C(11)–C(12)	116.5 (3)	N(21)–C(21)–C(22)	126.2 (3)
N(11)–C(11)–C(16)	125.5 (3)	N(21)–C(21)–C(26)	116.5 (3)
C(11)–C(12)–C(13)	122.8 (3)	C(21)–C(22)–C(23)	121.3 (3)
C(12)–C(13)–C(14)	119.7 (3)	C(22)–C(23)–C(24)	120.6 (3)
C(13)–C(14)–C(15)	118.0 (3)	C(23)–C(24)–C(25)	118.1 (3)
C(14)–C(15)–C(16)	120.7 (3)	C(24)–C(25)–C(26)	120.1 (3)
C(15)–C(16)–C(11)	120.8 (3)	C(25)–C(26)–C(21)	122.7 (3)
C(16)–C(11)–C(12)	117.8 (3)	C(26)–C(21)–C(22)	117.3 (3)
C(13)–C(14)–N(12)	121.1 (3)	C(23)–C(24)–N(22)	121.3 (3)
C(15)–C(14)–N(12)	120.9 (3)	C(25)–C(24)–N(22)	120.7 (3)
C(14)–N(12)–C(17)	121.8 (3)	C(24)–N(22)–C(27)	121.5 (3)
C(14)–N(12)–C(18)	122.0 (3)	C(24)–N(22)–C(28)	122.1 (3)
C(17)–N(12)–C(18)	116.0 (3)	C(27)–N(22)–C(28)	116.2 (3)

Zn complex is via the nitroso oxygen atom, as is the case for the Sn complex;[5] the Co complex, which has tetrahedral coordination,[4] is bonded via the nitroso nitrogen atom. The Pd complex is also bonded through nitrogen.

The structure of the free 4-nitroso-*N*,*N*-dimethylaniline ligand is disordered,[13] as is that of the equivalent diethyl compound.[14] The latter structure was determined at −165 °C and is more accurate even though it contains two independent molecules in the asymmetric unit.

The changes in bond lengths from the free ligand to the complexed ligand are generally marginally larger than the esd's and show a trend toward the quinoid structure, which is presumably associated with the change in color upon complexation. The largest changes are for the N=O (+0.070 Å) and C—N (−0.075 Å) bonds for the compound reported here.

Several modes of binding of RN=O ligands to transition metals, such as monodentate N binding, a bridging configuration involving both of the nitroso atoms, N,O chelate binding and monodentate O binding have either been observed or proposed. Monodentate O binding was proposed in the tetrahedral structure $\mathrm{CoCl_2[(CH_3)_2NC_6H_4NO]_2}$,[4] but upon investigation, this structure showed monodentate N binding to be present rather than the proposed O binding. The ν(N=O) assignment in this cobalt complex is 1499 cm^{-1}.[4]

This slightly lower nitroso stretching frequency, relative to the free ligand ν(N=O) (1528 cm^{-1}, KBr disk), is consistant with the small observed changes in ligand geometry that accompany metal coordination. A comparison of the IR spectra of 4-nitroso-*N*,*N*-dimethylaniline (free ligand) and dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II) showed a similar shift, and decrease in intensity, in the nitroso stretching frequency from 1528 cm^{-1} (free ligand) to 1498 cm^{-1} (complexed ligand).

An absorption present at 1564 cm^{-1} in the Zn complex is assigned to the $\nu(\mathrm{C}\overset{-}{\cdots}\mathrm{C})$ vibration associated with the phenyl ring participating in extended conjugation. This same absorption is present in 4-nitroso-*N*,*N*-dimethylaniline, 4-nitroso-*N*,*N*-diethylaniline, and their corresponding Zn and Pd complexes,[16] all to within 10 cm^{-1}. This absorption is also present in dimethylaniline[16] (1570 cm^{-1}) in which no ν(N=O) is possible, suggesting an error in the original assignment of a peak at 1560 cm^{-1} in the Sn complex to ν(N=O).[5] It would seem more likely that a peak at 1501 cm^{-1} in the Sn complex is due to ν(N=O) and the peak at 1560 cm^{-1} should be assigned to $\nu(\mathrm{C}\overset{-}{\cdots}\mathrm{C})$. It is likely that the absorption at 1560 cm^{-1} is shifted as a result of the phenyl ring conjugation being extended as compared to dimethylaniline and diethylaniline, in which only the dialkylamino nitrogen is present to extend conjugation.

Correlation charts of N–O bond distances and wavenumbers ($\bar{\nu}$) of the ω(N=O) mode predict an IR absorption at approximately 1380 cm^{-1} for the ω(N=O) vibration in 4-nitroso-*N*,*N*-dimethylaniline.[11] The infrared spectrum of this compound shows two medium–strong absorptions near this value, one at 1398 cm^{-1} and the other at 1366 cm^{-1}. When complexing to the zinc atom through the nitroso oxygen takes place, the ω(N=O) vibration should shift to a much lower wavenumber if this wagging vibration remains. Yet, upon complexation to the zinc atom, neither of these peaks shifts more than 5 cm^{-1}, suggesting an error in the as-

Table IV. IR Spectral Data for Selected Complexes (from 1600–1150 cm^{-1})

$\mathrm{(CH_3)_2NC_6H_4NO}$	$\mathrm{ZnCl_2[(CH_3)_2NC_6H_4NO]_2}$	$\mathrm{SnCl_2(CH_3)_2[(CH_3)_2NC_6H_4NO]_2}$	$\mathrm{PdCl_2[(CH_3)_2NC_6H_4NO]_2}$
1603 (s)	1610 (s)	1614 (s)	1608 (s)
1552 (m)	1564 (m)	1561 (m)	1558 (s)
1528 (s)			1528 (w)
	1498 (w)	1501 (w)	1505 (m)
1445 (m)	1458 (w)	1456 (w)	1460 (w), 1445 (w)
1398 (s)	1400 (s)	1397 (m)	1408 (m), 1389 (m)
1366 (s)	1371 (m)	1370 (w)	1363 (m)
1337 (s)	1341 (m)	1335 (s)	1338 (m)
1302 (s)	1304 (s)	1302 (s)	1318 (m)
1235 (s)			1230 (w)
			1172 (vs)
			1160 (s)

signment of ω(N=O) vibrations in terminal nitroso compounds.

Also of interest is a strong IR absorption at approximately 1235 cm^{-1} for 4-nitroso-*N*,*N*-dimethylaniline. When the ligand complexes to Zn, this peak is no longer present at the previous frequency and appears to have either been eliminated or has shifted into the region of a broad absorption band centered at approximately 1150 cm^{-1}. A large shift to lower frequency or an annihilation of this peak upon complexing would be expected to happen to the ω(N=O) motion upon complexing through the nitroso oxygen.

At present it appears that no conclusive correlation between IR spectroscopy and arylnitroso ligand binding characteristics can be assumed.

Acknowledgment. We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada for an operating grant to B.E.R. and R.J.B., the University of Regina for computing time, and H. Wang for assistance with computing.

Registry No. ZnCl$_2$[(CH$_3$)$_2$NC$_6$H$_4$NO]$_2$, 123265-48-5; SnCl$_2$(CH$_3$)$_2$[(CH$_3$)$_2$NC$_6$H$_4$NO]$_2$, 82286-88-2; PdCl$_2$[(CH$_3$)$_2$NC$_6$H$_4$NO]$_2$, 63527-61-7; [(CH$_3$)$_2$NC$_6$H$_4$NO]$_2$, 138-89-6.

Supplementary Material Available: Table B, listing crystal data and experimental parameters, Table C, listing anisotropic thermal parameters for the non-hydrogen atoms, Table D, listing bond lengths involving hydrogen atoms for dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II), Figure A, showing relevant IR spectra, and Figure B, showing bond length differences in the ligand (6 pages); Table A, listing observed and calculated structure amplitudes for dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II) (19 pages). Ordering information is given on any current masthead page.

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Q-Band Splitting in the Spectra of Heme Proteins

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Received June 22, 1988

The origin of Q-band splitting and line broadening in the electronic absorption spectra of certain types of heme proteins has remained an unsolved problem, despite having been documented for many years.[1] Recently, we have found that certain metalloporphyrin-modified myoglobins[2-4] exhibit Q-band splittings, and we have performed studies to elucidate the origin of this effect. In this paper we first focus attention on the details of the absorption spectra of modified sperm whale myoglobin (Mb), noting the possible contributors to Q-band perturbation and outlining experiments designed to select among these factors. We then attempt to explain the general observation of Q(0,0)-band splitting in hemes.

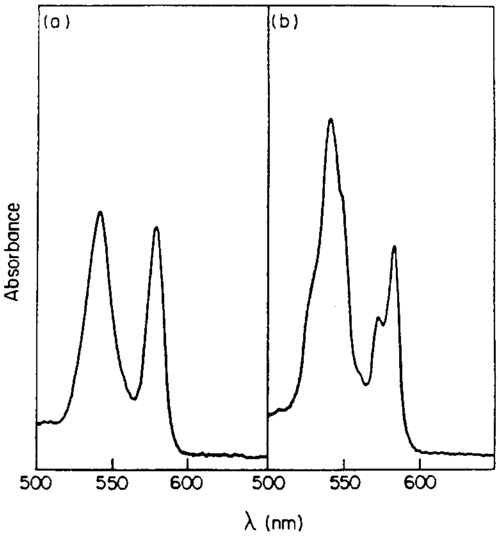

Figure 1. Q-band region in the electronic absorption spectra of (a) magnesium mesoporphyrin IX dimethyl ester (+ imidazole) in CH$_2$Cl$_2$ and (b) MgMb in μ = 0.1 M aqueous sodium phosphate buffer (pH 7.0, 22-24 °C). The absorbance scales for the spectra are similar but not identical.

Table I. Porphyrin Absorption Spectral Data[a]

	MP-DME		MP-DME + py[b]		MP-diacid/protein	
M	λ, nm	rel OD	λ, nm	rel OD	λ, nm	rel OD
Mg	397	1.0	411	1.0	409	1.0
	524	0.041	529	0.046	542	0.037
	561	0.070	562	0.032	584 (573 sh)	0.022
Zn	400	1.0	412	1.0	414	1.0
	531	0.046	514	0.052	541	0.047
	568	0.066	577	0.040	583 (573 sh)	0.024
Cd	406	1.0	419	1.0	421	1.0
	541	0.085	550	0.072	551	0.076
	576	0.066	585	0.031	591 (582 sh)	0.027
Pt	380	1.0	380	1.0	380	1.0
	498	0.078	499	0.079	499	0.052
	535	0.161	535	0.161	534	0.172
Pd	392	1.0	392	1.0	391	1.0
	511	0.073	511	0.074	510	0.083
	546	0.229	546	0.231	544	0.235
H$_2$	398	1.0	398	1.0	395	1.0
	497	0.084	497	0.084	496	0.080
	531	0.058	531	0.063	532	0.058
	567	0.039	567	0.042	562	0.042
	620	0.028	620	0.030	614	0.030
Sn	404	1.0	407	1.0	404	1.0
	537	0.081	538	0.084	537	0.050
	574	0.071	575	0.077	577 (569 sh)	0.031

[a] Reference 4. P = mesoporphyrin IX; MP-DME spectra were measured in CH$_2$Cl$_2$ solution; protein spectra were measured in μ = 0.1 M sodium phosphate buffer (22-24 °C). For each metal derivative, the peak intensities for the absorption bands are given as a ratio relative to the Soret (OD = 1.0). This is to facilitate comparison of data for each metal derivative. The ratios are not intended to be used between metal derivatives; that is, the Soret bands for the metal Mb complexes do not have exactly the same extinction coefficients. [b] Magnesium mesoporphyrin IX was titrated with imidazole in order to give a five-coordinate species.[10]

Consider the three major contributors to perturbations in a porphyrin absorption spectrum. First, minor changes in both the λ_{max} of the Soret and Q bands, and their relative intensities, can arise due to differences in the polarity of the porphyrin environment.[5] Second, aggregation of porphyrin units[6] can lead to shifts and line broadening of absorption bands due to dipolar coupling between the chromophores.[7] Third, larger perturbations in both the position of λ_{max}, and the relative intensities of each of the absorption bands, can arise from changes in the coordination geometry of the porphyrin (for example, a change from four- to five-coordination or a change in the σ- or π-bonding character of the axial ligand).[5] The perturbations observed in the shapes

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