

Electronic Structure of N–S Compounds. A CNDO Study of Transition Metal Thionitrosyl Complexes $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$ and $\text{Pd}(\text{S}_2\text{N}_2\text{H})_2$

S. MILLEFIORI, A. MILLEFIORI

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125 Catania, Italy

and

G. GRANOZZI

Istituto di Chimica Generale ed Inorganica, Università di Padova, via Loredan 4, 35100 Padua, Italy

Received September 1, 1980

Conformational preferences, valence molecular orbitals and electronic charge distribution in thionitrosyl complexes $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$ and $\text{Pd}(\text{S}_2\text{N}_2\text{H})_2$ have been studied by means of CNDO calculations. Both complexes are predicted to exist in the cis conformation, in agreement with the experimental data. Valence molecular orbital energies and compositions show that covalent interactions between transition metal and ligand are important for the metal–ligand bonding. The population analysis gives evidence of inequivalent nitrogen and sulfur atoms and of rather polar S–N bonds in the planar ring. The charge distribution is tentatively correlated with the available experimental XPS binding energies.

Introduction

The peculiar structural and physical properties of inorganic N–S compounds [1–3] have prompted several studies on their electronic structure [4–6]. The knowledge of the N–S bond polarity and the nature of the valence molecular orbitals (MOs) are both of particular importance to a better understanding of the N–S bond properties. Several theoretical works have been done to this end, but their results often disagree with each other. As an example, *ab initio* calculations give in N_4S_4 a N–S charge separation of about 0.55 e [7], while semi-empirical methods indicate a smaller charge separation [8]. Experimental works of particular relevance in the present context are those dealing with X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS, respectively), but they are rather scant. They are confined to the study of N_4S_4 [5, 9], N_2S_2 [10], $\text{S}_4\text{N}_4\text{O}_2$, $\text{S}(\text{NSO})_2$, $\text{S}_3\text{N}_2\text{NCOCCI}_3$ [5], to some S_3N_2 ring derivatives [6] and to cyclic sulfur imides of general structure $\text{S}_{8-x}(\text{NH})_x$ [11].

The present work is a CNDO study of the electronic structure of square planar thionitrosyl complexes $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$ and $\text{Pd}(\text{S}_2\text{N}_2\text{H})_2$ (Fig. 1). These compounds are of interest because of the *cis–trans* conformational problem they show, and the presence of inequivalent N and S atoms in a planar five-membered ring. Quite recently two XPS studies appeared on the Ni complex [12] and on both complexes [13]. They are of particular interest to the present study.

Calculations

Molecular orbital calculations were carried out within a CNDO scheme parametrized as reported in ref. 14. Previously it was usefully applied to the study of square-planar Ni(II) complexes [15, 16]. The experimental X-ray crystal structures of the complexes [17], slightly idealized to give a C_{2v} molecular symmetry (Fig. 1), were used throughout the calculations. The molecule was arranged in the yz plane, with the z-axis along the C_2 axis. The adopted N–H bond length of 1.05 Å is a mean N–H distance taken from the neutron diffraction structure of $\text{S}_4\text{N}_4\text{H}_4$ [18].

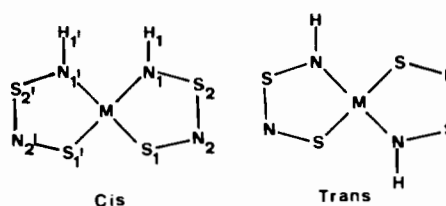


Fig. 1. Numbering system and geometries of thionitrosyl complexes. Ni–N₁ = 1.877; Ni–S₁ = 2.144; N₁–S₂ = 1.593; S₁–N₂ = 1.641; N₂–S₂ = 1.584; N₁–H₁ = 1.050; Pd–N₁ = 2.070; Pd–S₁ = 2.270; N₁–S₂ = 1.580; S₁–N₂ = 1.675; N₂–S₂ = 1.550; N₁–H₁ = 1.050; <Ni = <Pd = 90°; <N = 120°; <S = 105°.

Results and Discussion

Molecular Conformation

The investigated Ni and Pd thionitrosyl complexes were reported to exist in the *cis* conformation in the solid state [17]. Chemical evidence also supports this structure in solution. In fact a series of bridged derivatives of these complexes can be prepared by the substitution of the two hydrogen atoms of the imido groups in *cis* position [19].

The calculated total energies of the *cis* and *trans* conformers indicate that the *cis* structure is favoured over the *trans* one by 73 and 62 kcal/mol in the Ni and Pd complex, respectively. This relatively high energy difference between the two conformers is in line with that found in N_4S_4 between the conformations defined by coplanar N atoms or coplanar S atoms: 334 kcal/mol by *ab initio* calculations [7], 200 kcal/mol by CNDO/BW calculations [20]. It seems, therefore, to be peculiar of such a class of compounds to show noticeable energy difference between the various conformers. Because of the relatively high polarity of the bonds in the investigated compounds (*vide infra*), it is quite reasonable to suppose that electrostatic interactions contribute significantly to the stability of the *cis* conformation. Consequently, we have performed such type of calculations adopting the point charge interaction model [21]. The coulombic interactions were calculated according to the equation

$$E_{el} = \sum \frac{q_i q_j}{-r_{ij}}$$

where r_{ij} is the interatomic distance between atoms i and j , which bear the net charge q_i and q_j (see Table III), respectively. The procedure described in ref. 22 was followed, since the adopted model gives satisfactory results when the interacting charges are conveniently far apart. The results reported in Table I indicate that electrostatic interactions contribute by about 13 kcal/mol to the conformational preference in both complexes. The main *cis*-stabilizing contributions are associated with N_1-N_2' , S_2-S_1' and H_1-S_1' interactions, while destabilizing for the *cis* conformation are essentially N_2-N_2' and S_1-S_2' interactions. Interestingly the S_1-N_2' interaction is *cis*-stabilizing in the Ni complex, but it is *trans*-stabilizing in Pd complex. Minor details can be easily deduced from Table I. In the present compounds the major part of the conformational energy should probably reside in quite different orbital interactions between the two conformers.

Molecular Orbital Energies

The CNDO eigenvalue spectra of $Ni(S_2N_2H)_2$ and $Pd(S_2N_2H)_2$ are reported in Table II. Firstly we note several level crossings between the MOs in the two compounds. Moreover, MOs of the same symmetry

TABLE I. Calculated *Cis-Trans* Electrostatic Energy Differences in Thionitrosyl Complexes. ΔE in kcal/mol.

Couple	$Ni(S_2N_2H)_2$ ΔE (<i>cis-trans</i>)	$Pd(S_2N_2H)_2$ ΔE (<i>cis-trans</i>)
N_1-N_2'	-2.77×2	-2.28×2
N_1-S_2'	-0.23×2	-0.26×2
N_1-H_1'	-1.11×2	-0.93×2
N_2-N_2'	2.81	0.75
S_2-N_2'	-1.74×2	-1.39×2
S_1-N_2'	-0.36×2	2.31×2
H_1-N_2'	0.19×2	0.11×2
$H_1'-N_2'$	-0.52×2	-0.62×2
S_2-S_2'	3.32	3.49
S_2-S_1'	-2.44×2	-3.58×2
S_2-H_1'	1.13×2	1.42×2
H_1-S_1'	-1.94×2	-3.36×2
H_1-S_1	-0.24×2	-0.48×2
H_1-H_1'	0.85	1.01

do not show the same atomic orbital composition. The most noticeable differences appear in the $8b_2$ and $9a_1$ MOs, which both display noticeable d character in the Pd complex, while they are essentially N and S lone-pairs and $\sigma(S_1-N_2)$ -bonding MOs, respectively, in the Ni complex. The HOMO is the $4a_2$ MO in both compounds and it is mainly ligand in character with small contribution from d orbitals. It is well separated in energy from the next occupied MO which is again a ligand MO ($9b_2$, with 10% d_{yz}) in $Ni(S_2N_2H)_2$, but it is a MO of mixed composition ($4b_1$) in $Pd(S_2N_2H)_2$, showing metal-ligand π -bonding and N_1-S_2 covalent interactions. The highest-lying MO showing metal-ligand π -bonding interaction through metal d orbitals is a rather inner MO ($3b_1$). This seems to appear as a different feature from that found in square-planar $Ni(acac)_2$ complex, where CNDO calculations predicted the $Ni(3d)$ -ligand bonding interaction (of σ type) appreciably contributing to the highest filled MOs [15]. MOs with essentially nd character are predicted to lie in the intermediate region (10 - 12 eV) of the valence eigenvalue spectrum. Their position, however, in an UPS experiment is strongly determined by differential relaxation effects, which are particularly important for d metal-like MOs compared with those associated with ligand MOs [23, 24]. The seven lowest-lying levels are essentially S,N s-type MOs and are not reported in Table II.

Population Analysis

Charge distribution and Wiberg bond orders are reported in Table III. It is worth noting that the present results differ from those previously reported [12, 13], which are obtained by CNDO/2 calculations on the free ligand. Consequently, if XPS core binding energy assignments are based on the atomic net charges, some differences with the reported assignments [12, 13] can be anticipated.

TABLE II. Valence Molecular Orbitals of *cis* Thionitrosyl Complexes^a. Energies in eV.

Ni(S ₂ N ₂ H) ₂			Pd(S ₂ N ₂ H) ₂		
Orbital	Energy	Composition	Orbital	Energy	Composition
1b ₁	-15.95	π b delocalized	4b ₂	-16.43	σ b(N-H), n(N ₂)
4b ₂	-15.46	σ b(N-H), n(N ₂)	5a ₁	-15.85	n(N, S)
5a ₁	-15.20	n(N, S)	5b ₂	-14.94	n(N, S)
1a ₂	-14.75	π b ligand	1b ₁	-14.40	π b delocalized
6a ₁	-14.51	σ b(N ₁ -S ₂ , S ₁ -N ₂)	1a ₂	-14.09	π b ligand
5b ₂	-14.29	σ b(N ₂ -S ₂)	6a ₁	-14.03	σ b(N ₂ -S ₂ , N-H)
2b ₁	-11.50	Ni d _{xz}	2b ₁	-11.60	π b(Pd-N ₁ -S ₂ , S ₁ -N ₂)
2a ₂	-10.98	Ni d _{xy}	6b ₂	-11.30	σ b(N-H, N ₂ -S ₂)
7a ₁	-10.93	Ni d _{x²-y²} , d _{z²}	7a ₁	-10.98	Pd d _{z²} , d _{x²-y²} , σ b(S ₁ -N ₂)
8a ₁	-10.49	Ni d _{z²} , d _{x²-y²}	2a ₂	-10.83	Pd d _{xy}
6b ₂	-10.32	σ b(N-H, N ₂ -S ₂)	8a ₁	-10.69	Pd d _{x²-y²}
9a ₁	-10.16	σ b(S ₁ -N ₂)	7b ₂	-10.46	σ b(Pd-N), n(S ₁)
7b ₂	-9.42	σ b(Ni-N, S ₁ -N ₂)	9a ₁	-10.37	Pd d _{z²}
3a ₂	-8.95	π b(N ₁ -S ₂ , S ₁ -N ₂)	3a ₂	-9.98	π b(N ₁ -S ₂ , S ₁ -N ₂)
3b ₁	-8.83	π b(N ₁ -S ₂ , S ₁ -N ₂ , Ni d _{xz} -S ₁)	3b ₁	-9.56	π b(Pd d _{xz} -S ₁ -N ₂ , N ₁ -S ₂)
10a ₁	-8.68	σ b(N ₂ -S ₂)	8b ₂	-9.23	σ b(S ₁ -N ₂)Pd d _{yz}
8b ₂	-7.79	n(N, S)	10a ₁	-9.07	σ b(N ₂ -S ₂), n(N ₁)
4b ₁	-6.84	π b(Ni p _x -N ₁ -S ₁ , N ₂ -S ₂)	11a ₁	-8.19	n(S ₁)
11a ₁	-6.64	n(S ₁)	9b ₂	-7.42	σ b(N ₂ -S ₂), n(S ₁)
9b ₂	-6.05	n(S ₁), σ b(N ₂ -S ₂), Ni d _{yz}	4b ₁	-6.66	π b(Pd p _x -N ₁ -S ₁ , S ₂ -N ₂)
4a ₂	-5.16	n(N ₁ , S ₁), π b(N ₂ -S ₂)	4a ₂	-5.59	π b(N ₂ -S ₂), n(N ₁ , S ₁)
virtual					
5b ₁	1.57	π a(N-S)	5b ₁	0.75	π a(N-S)
5a ₂	1.81	π a(N-S)	5a ₂	0.96	π a(N-S)
10b ₂	3.41	d(Ni)	10b ₂	1.45	d(Pd)

^aTo facilitate comparisons, metal d orbitals are not referred to the axis-system of Fig. 1, but they are labelled following usual notations.

n = non bonding; b = bonding; a = antibonding.

TABLE III. Population Analysis in Thionitrosyl Complexes.

	s	p _x	p _y	p _z	d	Net charge	Bond order
Ni(S ₂ N ₂ H) ₂							
Ni	0.584	0.293	0.252	0.274	8.79	-0.193	Ni-N ₁ = 0.542
N ₁	1.287	1.583	1.150	1.226		-0.286	Ni-S ₁ = 0.917
N ₂	1.451	1.288	1.620	1.253		-0.612	N ₁ -S ₂ = 1.161
S ₁	1.567	1.516	1.023	1.565		0.329	N ₂ -S ₂ = 1.340
S ₂	1.518	1.475	1.333	1.100		0.574	S ₁ -N ₂ = 1.181
H	0.906					0.094	N ₁ -H = 0.931
Pd(S ₂ N ₂ H) ₂							
Pd	0.610	0.181	0.409	0.399	9.06	-0.658	Pd-N ₁ = 0.789
N ₁	1.257	1.715	1.088	1.172		-0.232	Pd-S ₁ = 0.878
N ₂	1.557	1.204	1.569	1.220		-0.550	N ₁ -S ₂ = 1.111
S ₁	1.670	1.378	0.956	1.454		0.542	N ₂ -S ₂ = 1.230
S ₂	1.611	1.623	1.305	0.998		0.463	S ₁ -N ₂ = 1.416
H	0.892					0.108	N ₁ -H = 0.955

The calculated net charges on Ni and Pd point out a great electron donating power of the planar N-S ring. The Pd atom shows a greater electron accepting power than Ni atom. The net charge values on Ni and

Pd seem to indicate an actual oxidation state of the two atoms next to O.

Inequivalent N and S atoms bear different net charges. In the Ni(S₂N₂H)₂ complex N₁ has less charge

than N_2 , while S_2 is more positively charged than S_1 . This is in agreement with the reported core binding energy assignments in this complex [12]. The noticeable difference between the N_1 and N_2 net charges seems to support the inferred [12] electron donating properties of N_1 toward Ni. In fact, in cyclic compounds such as N_4S_4 and $S_4N_4H_4$, in absence of extracyclic electron donating possibility, it was found [7, 25–27] that the net charges on bicoordinated and threecoordinated N atoms are nearly equal or somewhat higher in the latter.

In the Pd complex the same charge difference between N_1 and N_2 is maintained, so the same core binding energy assignment as in Ni complex should be valid, in contrast with the reported one [13]. In the Pd complex the net charge value on S_2 and S_1 atoms is reversed with respect to the Ni complex, the charge difference being also reduced, making their relative binding energy assignment less straightforward than in $Ni(S_2N_2H)_2$.

Bond orders indicate a partial double bond character for N_2-S_2 and S_1-N_2 bonds in the Ni and Pd complexes, respectively. Clearly there is not a relationship between S–N bond length (Fig. 1) and S–N bond order, as was also found in other cyclic S–N compounds [25].

Acknowledgements

This work was partially supported by C.N.R., Rome. We thank Prof. I. Fragalà for useful discussions.

References

- H. W. Roesky, *Advances in Inorganic Chemistry and Radiochemistry*, **22**, 239 (1979).
- H. W. Roesky, *Angew. Chem. Int. Ed.*, **18**, 91 (1979).
- M. M. Labes, P. Love and L. F. Nichols, *Chem. Rev.*, **79**, 1 (1979).
- P. Cassoux, O. Glemser and J. F. Labarre, *Z. Naturforsch.*, **32b**, 41 (1977).
- M. V. Andreocci, M. Bossa, V. Di Castro, C. Furlani, G. Mattogno and H. W. Roesky, *Z. Physik Chem., N.F.*, **118**, 137 (1979).
- M. V. Andreocci, M. Bossa, V. Di Castro, C. Furlani and G. Mattogno, *Gazz. Chim. It.*, **110**, 1 (1980).
- A. Millefiori and S. Millefiori, *J. Chem. Res. (S)*, 244 (1980).
- S. Millefiori and A. Millefiori, *Inorg. Chim. Acta*, **45**, L19 (1980).
- W. R. Salaneck, J. W-p Lin, A. Patan, C. B. Duke and G. P. Ceasar, *Phys. Rev.*, **B13**, 4517 (1976).
- D. C. Frost, M. R. Legeyt, N. L. Paddock and N. P. C. Westwood, *J. Chem. Soc. Chem. Comm.*, 217 (1977).
- A. Barrie, H. Garcia-Fernandez, H. G. Heal and R. J. Ramsay, *J. Inorg. Nucl. Chem.*, **37**, 311 (1975).
- M. Bossa, C. Furlani, G. Mattogno and E. Rampazzo, *Inorg. Chim. Acta*, **27**, L117 (1978).
- R. Grinter and J. D. Woollins, *Inorg. Chim. Acta*, **39**, 193 (1980).
- E. Tondello, *Inorg. Chim. Acta*, **11**, L5 (1974).
- I. Fragalà, L. L. Costanzo, E. Ciliberto, G. Condorelli and C. D'Arrigo, *Inorg. Chim. Acta*, **40**, 15 (1980).
- G. Condorelli, I. Fragalà, A. Centineo and E. Tondello, *Inorg. Chim. Acta*, **7**, 725 (1973).
- J. Weiss and U. Thewolt, *Z. Anorg. Allg. Chem.*, **363**, 159 (1968).
- T. M. Sabine and G. W. Co, *Acta Cryst.*, **23**, 574 (1967).
- See references cited in ref. 1.
- M. S. Gopinathan and M. A. Whitehead, *Can. J. Chem.*, **53**, 701 (1970).
- L. J. Collins and D. N. Kirk, *Tetrahedron Lett.*, 1547 (1970).
- J. Kao and L. Radom, *J. Amer. Chem. Soc.*, **101**, 311 (1979).
- I. H. Hillier, *Pure Appl. Chem.*, **51**, 2183 (1979).
- For a recent discussion on photoelectron spectra of d-metal compounds see also: C. Furlani and C. Cauletti, *Struct. Bonding (Berlin)*, **35**, 119 (1978).
- A. E. Foti, V. H. Smith, S. Kishner, M. S. Gopinathan and M. A. Whitehead, *Mol. Phys.*, **35**, 111 (1978).
- D. E. Salahub and R. P. Messmer, *J. Chem. Phys.*, **64**, 2039 (1976).
- A. Millefiori and S. Millefiori, to be published.

Note added in proof:

In agreement with the present theoretical results, recent experimental studies support the *cis* structure of the investigated complexes: J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc. Dalton*, 1910 (1980); D. B. Powell and J. D. Woollins, *Spectrochim. Acta*, **36A**, 447 (1980); D. T. Hawort, G. Y. Lyn, J. D. Brown and J. Chien, *Spectrochim. Acta*, **34A**, 371 (1978); I. S. Butler and T. Saway, *Can. J. Chem.*, **55**, 3838 (1977).

The appearance of further works on the electronic structure of N–S compounds is also acknowledged: W. von Niessen and G. H. F. Dierksen, *J. Electr. Spectr. Rel. Phenom.*, **20**, 95 (1980); R. H. Findlay, M. H. Palmer, A. J. Downs, R. G. Egdal and R. Evans, *Inorg. Chem.*, **19**, 1307 (1980); P. Brant, D. C. Weber, C. T. Ewing, F. L. Carter and J. A. Hashmail, *Inorg. Chem.*, **19**, 2829 (1980); R. C. Haddon, S. R. Wasserman, F. Wudl and G. R. J. Williams, *J. Am. Chem. Soc.*, **102**, 6687 (1980); M. Hojo, *Bull. Chem. Soc. Japan*, **53**, 2865 (1980).