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MO Studies for Transition Metal Complexes with Polydentate Ligands. IV[1]. On the Influence of the Macrocycle Size and Conjugation Extension in Co^{III} Complexes

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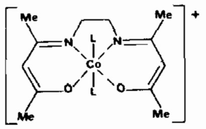
The effects of the enlargement of the equatorial ligand and of the extension of π-delocalization on the electronic structure and energy levels of a transition metal ion are examined by studying through SCCC–MO (self consistent in charge and configuration) calculations the bonding situation in Co^{III} complexes having different Schiff bases as equatorial ligands and equal nitrogen-containing bases as axial ligand. The reciprocal influence of different axial ligands with the same equatorial arrangement is also analysed. The metal charge and the σ and π overlap population of the metal-to-ligand bonds are not significantly affected, i.e. the extension of π bonding over a larger equatorial macrocycle does not enable more negative charge to be back-donated from metal to ligand. Then parallel physicochemical behaviours are suggested in agreement with experimental evidence.

The theoretical results on the corresponding complexes of Co^{II}, Ni^{II}, Pd^{II}, and Pt^{II} are also given.

Introduction

In recent years increasing attention has been payed to investigations on transition metal complexes which may be regarded as models of molecules of biological interest. In particular, cobalt complexes with tetradentate Schiff-bases like bae (1), salen (2) and saloph (3)* have been proposed as models of the Vitamin B_{12} compounds for the similar physico-chemical behaviour such as, *e.g.*, the ability to form stable organometallic compounds[2,3] and also as models of the naturally occurring oxygen-carriers for their capacity to take up molecular oxygen reversibly.[4] Experimental data on ground-state properties and thermodynamic and kinetic aspects of reactivity show a varying reciprocal influence of axial and equatorial ligands. These different interactions may be due to different bonding situations around the central metal atom. Therefore a theoretical investigation on their nature is in order.



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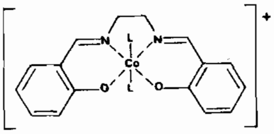

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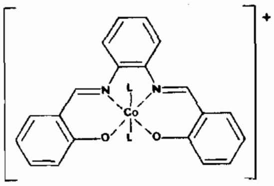

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Structural formulae

In addition to σ bonding, two properties of the equatorial ligand are presumed to play an important role in determining the electronic distribution on the central metal atom: 1) the extension of the π-electron conjugation, and 2) the nature and arrangement of the donor atoms. Here the attention is focused on the first point, while the second factor will be discussed in a following paper.[5]

If the π-electron system of the polydentate ligand is regarded to act as an electron reservoir, then an enlargement of the π system could cause a more marked «back-donation» effect from the central metal atom to the equatorial ligand and consequently an increasing electron-release from the axial ligand. The first effect should be responsible of a greater involvement of the «out-of-plane» metal orbitals (d_{xz}, d_{yz}, and p_z) in the metal-to-ligand (equatorial) bonding and hence of a greater stabilization of the complex. On the other side, the second effect should be reflected in different donor power and consequently in different reactivity of the same axial ligand.

(*) Bae = NN'—ethylenebis(acetylacetoneiminato) dianion; salen = NN'—ethylenebis(salicylideneiminato) dianion; saloph = NN'—*o*-phenylenebis(salicylideneaminato) dianon.

(1) Part III, G. De Alti, V. Galasso and A. Bigotto, *Inorg. Chim. Acta*, *4*, 267 (1970).

(2) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev.*, *4*, 41 (1970)

(3) G. Schrauzer, *Accounts Chem. Res.*, *1*, 97 (1968); H.A.O. Hill, J.M. Pratt and R.J.P. Williams, *Discuss, Faraday Soc.*, *47*, 165 (1969).

(4) C. Floriani and F. Calderazzo, *J. Chem. Soc.* (A), 1969) 946; A.L. Crumbles and F. Basolo, *J. Amer. Chem. Soc.*, *92*, 55 (1970); G. Amiconi, M. Brunori, E. Antonini, G. Tauzher and G. Costa, *Nature*, *228*, 549 (1970).

(5) Part V, G. De Alti, V. Galasso and A. Bigotto, *Inorg. Chim. Acta*, *6*, 153 (1972).

In order to investigate these aspects we have considered octahedral cobalt complexes with the quoted macrocycle equatorial ligands and two nitrogen-containing bases in the axial positions. By virtue of complex formation the ligands form two six-membered rings,—each consisting of cobalt, two donor atoms (oxygen and nitrogen) and three carbon atoms with sp^2 hybridization,—connected by the cobalt atom. At first sight, then, extensive delocalization of the π electrons encompassing the entire complex is expected to occur through p_π—p_π and d_π—p_π bonding. The theoretical analysis of the metal-ligand interactions should provide some useful informations for the chemists involved in investigating the more complex biological systems.

For large molecules like those here considered *ab-initio* calculations are, with present technology, completely out of question. Semiempirical approximate methods must then be used. The results so obtained are not to be given an absolute value, bearing significance only when used in interpreting *relative* electronic properties.

Details of calculation

The geometry of the equatorial macrocycle in the bae and salen complexes has been assumed planar with distances and angles as close as possible to the experimental data on analogous derivatives.[6] The structure of the saloph derivative has been assumed to incorporate exactly that of the salen derivative. The nitrogen atom of the axial ligand has been located at the distance of 2 Å from the central metal atom (average value of the distances of several axial ligands). The equatorial ligand is assumed to lie in the xy plane, with the x axis bisecting the NCoN angle.

The computational technique has been the Ballhausen-Gray[7] traditional version of the Wolfsberg-Helmholz[8] method. For the purpose of MO calculations the Co and N/O atoms have been considered σ- and π-bonded while only π bonding within the macrocycle has been taken into account. Thus the orbital basis set used has been the 3d, 4s, and 4p orbitals of Co, the $2p\sigma$ and $2p\pi$ orbitals of N and O and the $2p\pi$ of the C atoms sharing the π conjugation.

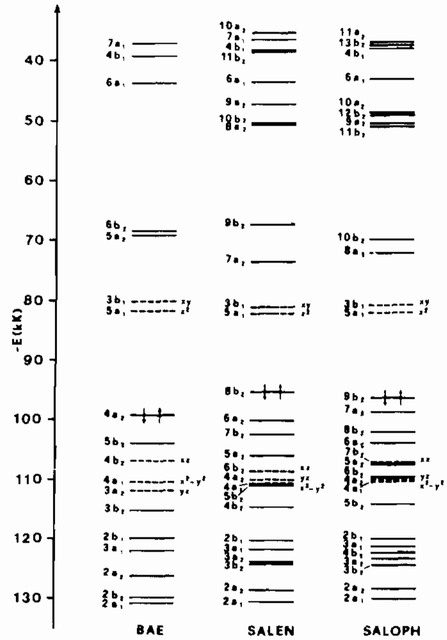
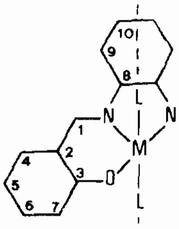


Figure 1. One-electron energy level diagram for Co^{III} complexes.

Table I. Electronic population of metal orbitals and atomic net charges for Co^{III} complexes.

Complex	BAE				SALEN				SALOPH			
Case	A	B	C	D	A	B	C	D	A	B	C	D
3d	7.8200	7.8370	7.8730	7.9250	7.8265	7.8442	7.8781	7.9295	7.8270	7.8447	7.8785	7.9296
4s	0.4844	0.4975	0.5062	0.5022	0.4842	0.4965	0.5049	0.5000	0.4835	0.4959	0.5043	0.4996
4p	0.3338	0.3285	0.3211	0.3170	0.3247	0.3205	0.3163	0.3166	0.3255	0.3213	0.3169	0.3171
Co	0.3617	0.3362	0.3000	0.2559	0.3645	0.3387	0.3005	0.2537	0.3638	0.3381	0.3002	0.2537
L	0.3935	0.4667	0.5772	0.7176	0.3954	0.4695	0.5822	0.7289	0.3949	0.4689	0.5815	0.7288
N	0.0525	0.0125	−0.0465	−0.1157	0.2079	0.1662	0.1044	0.0308	0.1878	0.1461	0.0847	0.0120
C_1	0.2856	0.2831	0.2779	0.2673	0.2509	0.2485	0.2437	0.2328	0.2674	0.2648	0.2596	0.2472
C_2	−0.1483	−0.1484	−0.1484	−0.1485	−0.0374	−0.0372	−0.0370	−0.0364	−0.0387	−0.0385	−0.0383	−0.0376
C_3	0.2497	0.2480	0.2447	0.2380	0.1414	0.1408	0.1395	0.1368	0.1454	0.1447	0.1433	0.1401
O	−0.5139	−0.5300	−0.5549	−0.5868	−0.5926	−0.6079	−0.6315	−0.6617	−0.5925	−0.6078	−0.6313	−0.6614
C_4					0.0319	0.0314	0.0304	0.0277	0.0354	0.0349	0.0338	0.0307
C_5					−0.0403	−0.0403	−0.0404	−0.0405	−0.0403	−0.0403	−0.0405	−0.0405
C_6					0.0505	0.0500	0.0489	0.0462	0.0542	0.0536	0.0524	0.0494
C_7					−0.0616	−0.0616	−0.0617	−0.0621	−0.0615	−0.0615	−0.0616	−0.0621
C_8					−0.0286	−0.0287	−0.0289	−0.0294	0.0299	0.0298	0.0297	0.0295
C_9									−0.0375	−0.0374	−0.0372	−0.0367
C_{10}									−0.0264	−0.0264	−0.0263	−0.0263



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(6) S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Chem. Comm.*, *1970* 152; M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc.* (A), 2720.

(7) C.J. Ballhausen and H.B. Gray, « Molecular Orbital Theory », W.A. Benjamin Inc., New York, 1964.

(8) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, *20*, 837 (1952).

(9) J.W. Richardson, W.C. Nieuwpoort, R.R. Powell and W.F. Edgell, *J. Chem. Phys.*, *36*, 1057 (1962); J.W. Richardson, R.R. Powell and W.C. Nieuwpoort, *ibid.*, *38*, 796 (1963).

(10) E. Clementi and D.L. Raimondi, *J. Chem. Phys*, *38*, 2686 (1963).

Table II. Partial and total overlap populations for Co-L, Co-(N,O), C-N and C-O bonds in Co^{III} complexes

Complex	Bond	Case	A	B	C	D
BAE	Co-L		0.4794	0.4989	0.5098	0.4984
	Co-$(N,O)_\sigma$		0.9404	0.9298	0.9064	0.8691
	Co-$(N,O)_\pi$		0.1145	0.1120	0.1085	0.1058
	Total		1.5343	1.5407	1.5247	1.4733
	C-N		0.4770	0.4757	0.4765	0.4751
	C-O		0.2219	0.2262	0.2251	0.2266
SALEN	Co-L		0.4836	0.5035	0.5166	0.5067
	Co-$(N,O)_\sigma$		0.9382	0.9266	0.9040	0.8664
	Co-$(N,O)_\pi$		0.1009	0.0989	0.0969	0.0970
	Total		1.5227	1.5290	1.5275	1.4701
	C-N		0.5225	0.5225	0.5221	0.5193
	C-O		0.1304	0.1303	0.1299	0.1284
SALOPH	Co-L		0.4828	0.5027	0.5149	0.5054
	Co-$(N,O)_\sigma$		0.9375	0.9259	0.9035	0.8661
	Co-$(N,O)_\pi$		0.0997	0.0976	0.0954	0.0947
	Total		1.5200	1.5262	1.5138	1.4662
	C-N		0.5248	0.5251	0.5251	0.5232
	C-O		0.1316	0.1315	0.1311	0.1293

The AO's have been taken from Richardson *et al.*[9] for Co^+ and from Clementi-Raimondi[10] for the other atoms. The pertinent VOIP's have been taken from Basch *et al.*[11]

In order to simulate different donating powers relative to the axial ligand, different values of energy have been assigned to its $2p\sigma$ orbital, namely 125, 114, 100, and 84.4 kK (Cases A, B, C, and D respectively).

In Table I are summarized the atomic charges and the metal orbital configurations, while the interatomic overlap populations are given in Table II. The one-electron MO level schemes for Case B are shown in Figure 1.

Discussion

Electronic Structure. The considered complexes are referred to as forming the series bae, salen and saloph in order of increasing size of the π system. The data in Table I bring out some interesting points when considered for a same donor power of the axial ligands, say *e.g.* Case B. First, the orbital configuration of Co stays sensibly constant; consequently, also the net charge carried by the central metal atom remains practically unaffected. Second, the atomic charge on the axial ligand displays no significant variation. Third, the equatorial chelating atoms undergo pronounced alterations: the oxygen atoms acquire a more negative charge and the nitrogen atoms become more positive. Furthermore, the carbon atoms at positions 2 and 3 (the atom numbering adopted is shown in Table I) lose some fraction of formal charge and so does also the carbon atom 1 to a less extent. Minor variations involve the remaining peripheral carbon atoms. Generally speaking, if variations occur at all, the largest ones originate on passing from bae to salen derivatives, a virtual constancy of figures being observed as the macrocycle enlarges from salen to saloph.

With regard to the overlap population (Table II) in the bonds around the central metal atom, two opposite trends can be distinguished through the series of complexes. On the one hand, both the σ and π overlap populations of the metal-to-equatorial ligand bond show a very slight lowering; on the other side the overlap population shared by the metal and the axial partner increases very slightly. These trends are reflected in a moderate decreasing of the total overlap population for the metal, indicating a relatively lower metal-to-ligand interaction on going from bae to saloph derivatives. As to the C–N and C–O bonds, the overlap populations may be diagnostic of a strengthening of the former and of a marked weakening of the second along the series. The different distances adopted for C–N bond in the bae and salen derivatives[6] (1.33 Å versus 1.29 Å) can be responsible of the increase in the relative overlap population, while the same variation of the C–O bond distances[6] (1.29Å-1.33Å) cannot be regarded as the main cause of the rather sensible lowering in the relative overlap population. Presumably, this decreasing is governed primarily by the enlargement of the equatorial macrocycle, which involves the carbon partner in aromatic conjugation to a greater extent and lowers then its participation in the C–O bond. In this way the $2p_z$ AO of oxygen could have more ability for coordinating one more cobalt atom to give a dimeric molecule. This would corroborate, on quantitative basis, the suggestion previously advanced for explaining experimental evidence on the crystalline state of $[EtCd^{III}(salen)]$.[6] In view of the close analogy between the salen and saloph derivatives, a similar possibility of forming dimeric molecules in the solid state may be anticipated also for the saloph compounds.

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(11) H. Basch, A. Viste and H.B. Gray, *Theoret. Chim. Acta*, *3*, 458 (1965).

Energy Diagrams. The two lowest empty MO's are always predicted to bear predominantly metal character, «d_{z^2}» the first and «d_{xy}» the second. The $4a_1$ MO is essentially $d_{x^2-y^2}$ metal in nature. The «d_{xz}» and «d_{yz}» MO's involve instead a considerable mixing with AO's of the equatorial ligand. As the macrocycle size progressively enlarges, the highest occupied MO's become built out exclusively of planar ligand orbitals of π nature. At the same time, the occupied «d» MO's tend progressively to lie more closely each to other. The energy gap between the highest filled and the first virtual MO's does not follow a regular trend. Indeed it decreases markedly on passing from bae to salen derivatives and then raises slightly on going from salen to saloph.

Variation of the Donor Power of the Axial Ligand. Looking at Table I, the following features are apparent for the atoms directly involved in the coordinate bond as the donor power of the axial ligand increases, i.e. on passing from Case A to case D. The positive charge decreases on Co and increases on the axial ligand. The oxygen atom displays a moderate increase of negative charge. A lowering of positive charge is undergone by the nitrogen atom so as to attain a formal negative charge for Cases C and D of the bae derivative.

As far as the interatomic overlap populations are concerned, the various contributions show slight but not regular variations. However, noteworthy is the fact that the C–N and C–O bond overlap populations appear not to be sensitive to the donor power.

Generally speaking, the energy level diagrams versus donating power show the same trends which operate in dimethylglyoximato (dmg) derivatives.[12] In particular the antibonding «d_{z^2}» MO raises its energy with concomitant loss of metal character and gain of axial ligand nature. With strong donors, «d_{z^2}» MO must be regarded as bonding MO which lies under the other bonding «d» MO's. This picture is consistent with the crystal-field theory because in such cases the axial ligand assumes a rather high positive charge which should stabilize the «d_{z^2}» MO.

Final remarks

A few conclusions can be drawn from this work:

(*a*) The enlargement of the macrocycle size and consequently the extension of the π electron conjugation do not affect significantly the net positive charge on the metal atom. In so far as is assumed a correlation between the central atom charge and the stability of the transition metal complex,* the present results suggest a comparable stability for the three considered complexes.

The comparable values experimentally established for the equilibrium constants of the deprotonation reactions of the corresponding diaquo-complexes[2] ($pK_1 = 6.86$ for salen and 6.73 for saloph derivatives) are consistent with the nearly same electron situation (atomic charges and bond overlap population) predicted for cobalt-to-axial ligand bond. The greater positive charge on the axial ligand ($+0.474$) and the greater overlap population of the axial ligand (0.541) found for the corresponding dmg complexes[12] are in agreement with the higher deprotonation equilibrium constant[13] ($pK_1 = 5.14$) of the corresponding dmg diaquo-derivatives and thus are diagnostic of a stronger coordinate bonding in dmg derivatives than in the complexes here considered.

The slightly different values in the experimental data pertinent to the present complexes may very presumably be attributable to different σ interactions** stemming from the equatorial ligands and/or to different deviations from planar geometry.

Although a direct correlation between the charge on cobalt and the ^{59}Co chemical shift has no theoretical basis,[14] it is worthwhile mentioning that there is some similarity between our results and NMR spectra.[15] Indeed for bae and salen complexes the calculated metal charge is almost the same ($+0.336$ and $+0.339$) and for their methyl derivatives ^{59}Co resonates at about the same magnetic field (CH_3Cobae: -7.3×10^3 ppm; $CH_3Co(bae)py$: -7.2×10^3 ppm; CH_3-Co(salen)H_2O: -7.2×10^3 ppm***),[15] whereas for dmg complex the calculated charge ($+0.288$)[12] and similarly the ^{59}Co resonance in the methyl derivative ($CH_3Co(dmg)_2py$: -3.6×10^3 ppm***)[15] are clearly different with respect to the bae and salen complexes.

(*b*) The σ and π bond overlap populations, and hence the total bond order, involving the metal-to-nitrogen and metal-to-oxygen bonds are not sensitive to the extension of π orbital network encompassing the entire complex. The π back-donation effect seems thus not to become more important with ring size enlargement. From the present theoretical approach, the arrangement and the nature of the chelating atoms as present in the smaller π system (bae) turn out to be mostly operative in determining the in-plane bonding situation around the central metal atom.

(*c*) Looking at the infrared frequency of a X–Y bond stretching mode as an approximate measure of the bond strength, the change in the frequency should be related primarily to change in π component if a constancy in σ component of the X–Y bond is assumed along the considered series of complexes. According to assignments made on empirical basis,[16] on

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* This assumption, which has no theoretical ground, follows from the finding by M. Zerner and M. Gouterman (*Theoret. Chim. Acta*, *4*, 44 (1966) that for metal porphyrins the order of increased observed stability corresponds to a calculated decrease in the metal charge.

(12) Part II, G. De Alti, V. Galasso, A. Bigotto and G. Costa, *Inorg Chim. Acta*, 3, 533 (1969).

** Preliminary calculations performed on $[Co^{III}(oiaphen)L_2]^+$ (oiaphen = NN'-ethylenebis-(α-methylsalicylideneaminato) dianion) by taking into account the inductive effect of the methl groups give moderately lower values of the positive charge on the axial ligand and of overlap population of the metal-to-axial ligand bond than in the unsubstituted species, in agreement with the experimental evidence[2]. This demonstrates the relative importance of the σ interactions, to which we are deserving further theoretical investigation.

*** Chemical shifts are relative to saturated aqueous solution of $K_3Co(CN)_6$.

(13) A.V. Ablov, B.A. Bovykin and N.M. Samus, *Zhur. neorg. Khim.*, *11*, 1832 (1966); *C.A.*, *65*, 17777 e (1966).

(14 J.S. Griffith and L.E. Orgel, *Trans. Faraday Soc.*, *53*, 601 (1957).

(15) H.A.O. Hill, G. Costa, G. Pellizer and A. Lowenstein, in "Magnetic Resonance in Biological Research", an International Conference, Cagliari, 1969.

(16) K. Ueno and A.E. Martell, *J. Chem.*, 59, 998 (1955); *60*, 1270 (1956).

Table III. Electronic population of metal orbitals, atomic net charges and overlap populations for Me-N, Me-O, C-N and C-O bonds in BAE derivatives.

Complex		Co^{II}	Ni^{II}	Pd^{II}	Pt^{II}
Configuration	nd	7.868	8.854	8.741	8.684
	(n+1)s	0.528	0.569	0.684	0.732
	(n+1)p	0.270	0.285	0.528	0.550
Charge	Me	0.334	0.292	0.047	0.034
	N	−0.049	−0.013	0.032	0.058
	O	−0.548	−0.540	−0.435	−0.408
	C_1	0.284	0.296	0.276	0.249
	C_2	−0.146	−0.145	−0.141	−0.141
	C_3	0.248	0.256	0.244	0.226
Overlap pop.	Me-N	0.673	0.735	0.910	0.952
	Me-O	0.393	0.403	0.637	0.672
	Total	1.066	1.138	1.547	1.624
	C-N	0.468	0.466	0.476	0.486
	C-O	0.228	0.228	0.230	0.232

passing from bae to salen analogs the C–N stretching undergoes a shift toward higher frequency while the C–O stretching moves in the opposite direction. These trends are shared by the π bond overlap populations (πOP) both of the C–N and C–O bonds:

		bae	salen
C–N	ν(cm^{-1})	1519	1533
	πOP	0.479	0.522
C–O	ν(cm^{-1})	1127	1087
	πOP	0.226	0.130

(*d*) The distribution of energy levels and their dependence on donor power of the axial ligand should provide some informations for a qualitative explanation of the trends of the redox process data. Indeed the present results anticipate that, other things being equal, the polarographic reduction should not be sensibly affected by a progressive enlargement of the macrocycle and should be controlled to an important extent by donor power of the axial ligand. This donor power influence is well reflected by the experimental data.[17] On the other side, the experiments also indicate a certain dependence on the macrocycle size but lower than that on the donor power. Different molecular distortions and/or different σ interactions (see footnote** on precedent page) may be responsible of this fact. Indeed, taking into account the methyl inductive effect, we could justify the easier reduction of salen in respect to oiaphen derivative.

Appendix

Calculations similar to those for Co^{III} have been performed also for the corresponding fully-planar complexes of the bivalent metal ions Co^{II}, Ni^{II}, Pd^{II}, and Pt^{II} by assuming the same structural parameters used for Co^{III}. As an example, a collection of the main results for the bae derivatives are presented in Table III and Figure 2.

For a given ligand the atomic charges, metal orbital configurations, overlap populations of the metal-to-ligand bonds as well as the energy diagrams parallel closely the results obtained for the corresponding dimethylglyoximato compounds.[1] Looking at the metal charge as an index of stability of the complex, these bivalent ions may be arranged in the order:

$$Co < Ni < Pd < Pt$$

in agreement with the stability order found experimentally by Maley and Mellor[18] for complexes of bivalent ions.

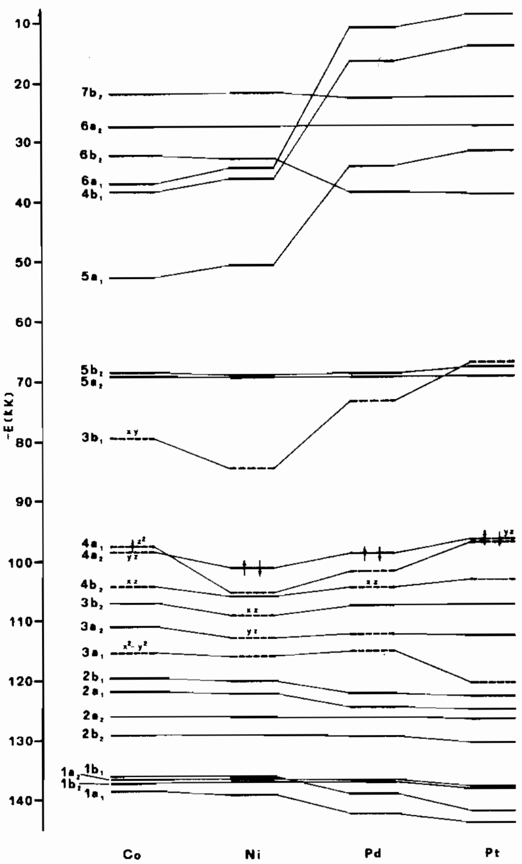

Figure 2. One-electron energy level diagram for bae complexes of bivalent metal ions.

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(17) G. Costa, G. Mestroni, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc.* (A), *1970* 2870.

The results obtained on the bae, salen and saloph derivatives of these metal ions indicate that the same arguments of Co cases are here transferable as far as the efficacy of the extension of π conjugation is concerned.

The net increase shown by the overlap population of the metal-to-oxygen and metal-to-nitrogen bonds on passing from Co^{II} to Pt^{II} is consistent with the trend found for the corresponding force constants.[19]

Acknowledgements. We wish to thank prof. G. Costa for stimulating discussion and the Consiglio Nazionale delle Ricerche of Italy for financial support.

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(18) L.E. Maley and D.P. Mellor, *Austral. J .Sci. Res.*, *2A*, 92 (1949).

(19 A. Bigotto, V. Galasso and G. De Alti, submitted for publication in Spectrochimica Acta.