Volume 21
Number 11
November 1982

Inorganic Chemistry

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On the Existence of Binuclear π-Bonded Dinitrogen Complexes

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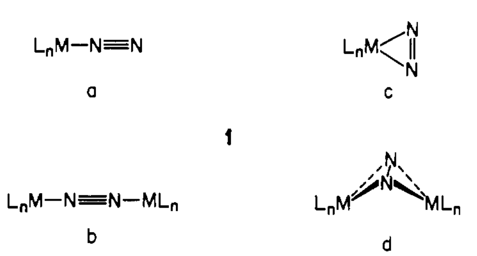
Received December 28, 1981

Comparative calculations on $Co_2(CO)_6(\mu\text{-}X_2)$, $X_2 = N_2, P_2, S_2^{2+}$, and especially C_2H_2, and also on the $Ni_2Ph_2(\mu\text{-}N_2)^{4-}$ core in the known lithiated side-on bonded complex indicate that there is nothing wrong with a side-on or π-bonded dinitrogen ligand in the $M_2L_6(\mu\text{-}N_2)$ system.

In nearly all known dinitrogen, N_2, transition-metal complexes, the diatomic fragment is coordinated in a σ or end-on manner, **1a** or **1b**. One or both N_2 lone pairs are thus used to form σ bonds to the metal.[1]



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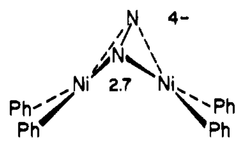
Side-on coordination, **1c** or **1d**, necessarily involving π bonding, is uncommon. Evidence has been presented for type **1c** bonding in $(\eta\text{-}C_5H_4R')_2Zr(N_2)R$, R′ = H or Me and R = $(Me_3Si)_2CH$.[1b] A recent crystal structure of a Ti_4 dinitrogen complex has N_2 in a complicated end-on and side-on bonded coordination.[1c] The binuclear bonding mode, **1d**, is found to date only in the two Jonas complexes[2] $[(PhLi)_6NiN_2(Et_2O)_2]_2$ and $[Ph(Na\cdot OEt_2)_2(Ph_2Ni)_2N_2NaLi_6(Et_2O)_4\cdot Et_2O]_2$. These are not simple molecules. As in other Li compounds, there is substantial phenyl–Li interaction in these. But if we extract the metal–N_2 core from the lithium ionic environment, we come to the basic $Ni_2Ph_4N_2^{4-}$ unit, **2**, a d^{10}–d^{10} complex. No doubt the Li atoms do contribute to the stability of the actual molecule. However, we think that a formal separation of them as Li^+ ions, made for purposes of comparison with other known complexes, is tenable.



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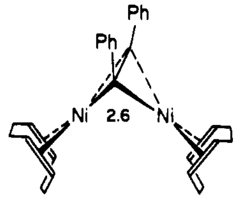

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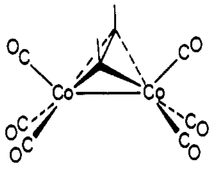
What is interesting about this formulation is there exist d^{10}–d^{10} binuclear complexes of the isoelectronic acetylene, e.g., $Ni_2(COD)_2(\mu\text{-}C_2Ph_2)$ (**3**)[3a] and related compounds,[3b] and these have structures that can be geometrically related to **2**.

This makes one think that one should seek other, as yet unknown, side-on bonded dinitrogen complexes, in structures similar to known dinuclear acetylene complexes. The $L_3M(\mu\text{-acetylene})ML_3$ class is particularly common,[4] e.g., $Co_2(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu_2)$ (**4**).[4a] On looking into the literature, one



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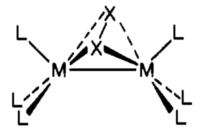

5

M = Fe, X = S,[5a] Se,[5b] NR[6]
M = CO, X = CR,[4] P,[7a] As[7b]

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(1) (a) See: Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625 and references therein. (b) Gynane, M. J. S.; Jeffery, J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 34–36. Jeffery, J.; Lappert, M. F.; Riley, P. I. *J. Organomet. Chem.* **1979**, *181*, 25–36. Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805–813. (c) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482–490.

(2) (a) Jonas, K. *Angew. Chem.* **1973**, *85*, 1050. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997–998. Krüger, C.; Tsay, Y.-H. *Angew. Chem.* **1973**, *85*, 1051–1052. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998–999. (b) Jonas, K.; Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Am. Chem. Soc.* **1976**, *98*, 74–81.

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(4) (a) Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774–1779. (b) Sly, W. G. *Ibid.* **1959**, *81*, 18–20. (c) Bonnett, J.-J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973–1976. (d) Bianchini, C.; Dapporto, P.; Meli, A. *J. Organomet. Chem.* **1979**, *174*, 205–212. (e) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923–1931. (f) Bailey, N. A.; Churchill, M. R.; Hunt, R.; Mason, R.; Wilkinson, G. *Proc. Chem. Soc., London* **1964**, *401*. Bailey, N. A.; Mason, R. *J. Chem. Soc. A* **1968**, 1293–1299. (g) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *J. Am. Chem. Soc.* **1972**, *97*, 6540–6541; *Inorg. Chem.* **1976**, *15*, 97–107. (h) Angoletta, M.; Bellon, P. L.; Demartin, F.; Sansoni, M. *J. Organomet. Chem.* **1981**, *208*, C12–C14. (i) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693–696. (j) Wang, Y.; Coppens, P. *Ibid.* **1976**, *15*, 1122–1127. (k) Mills, O. S.; Shaw, B. W. *J. Organomet. Chem.* **1968**, *11*, 595–699. (l) Restiva, R. J.; Ferguson, G.; Ng, T. W.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 172–176. (m) Ban, E.; Cheng, P.-T.; Jack, T.; Nyberg, S. C.; Powell, J. *J. Chem. Soc., Chem. Commun.* **1973**, 368–369. Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707–4716.

(5) (a) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1–11. (b) Campana, C. F.; Lo, F. Y.-K.; Dahl, L. F. *Ibid.* **1979**, *18*, 3060–3064.

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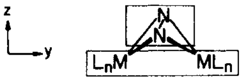
quickly finds that **4** is but one compound in an isoelectronic and isostructural series, **5**. With the P and As compounds[7] in this series, one is very close to a corresponding N_2 complex.[8]

The purpose of this paper is to examine what, if anything, is wrong with N_2 complexes analogous to **4** and **5**. We draw heavily on our recent work on the bonding of acetylenes in binuclear complexes.[9] Calculations were also performed on several members of the series **5** for comparison[10] and on complexes of type **2** and **3** as well. The calculations are of the extended Hückel type, with details given in the Appendix.

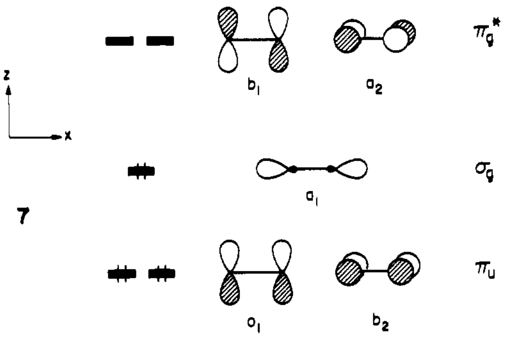
Orbitals of the Two Fragments

Fundamental to our analysis is a fragment approach, in which the complexes are built up as a composite of an L_nM-ML_n and X_2 piece, **6**. In this way, the differences in the interactions of the N_2 orbitals and those of the various other X_2 fragments can be explored.



6

The orbitals of a homonuclear diatomic are well-known. **7** illustrates the frontier orbitals of N_2, occupied $2\sigma_g$ and π_u and empty $\pi_g{}^*$. The orbitals are labeled in C_{2v}, in anticipation of complexation.



7

In the only two known structures where N_2 is found to bond side-on, the N–N bond length is stretched from its 1.10-Å length in free N_2 to 1.35 and 1.36 Å.[2] One would anticipate a similar elongation in any binuclear complex of N_2. Stretching the N–N bond would destabilize π_u, stabilize $\pi_g{}^*$, and, according to the calculations, stabilize $2\sigma_g$. But the general shape of the levels remains as in **7**.

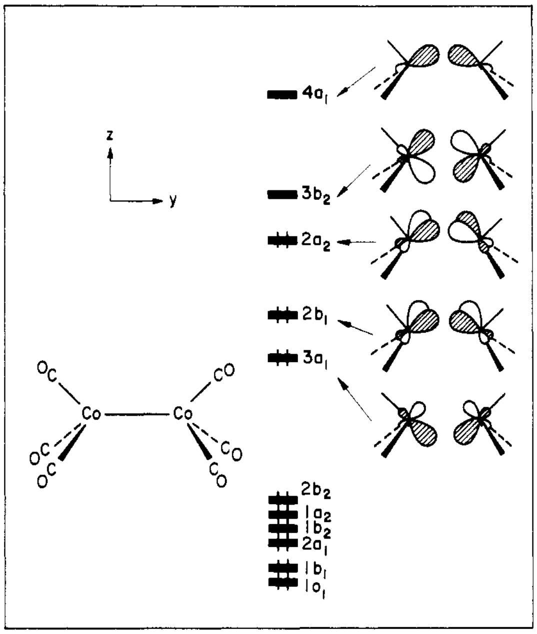
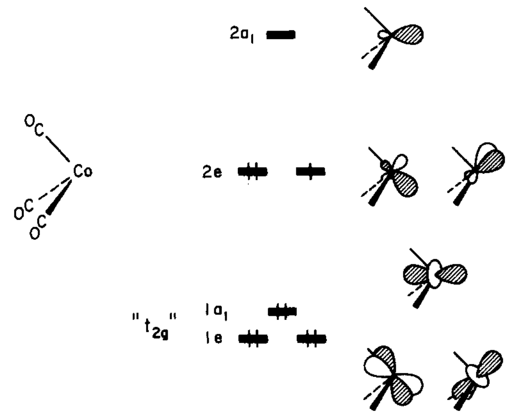


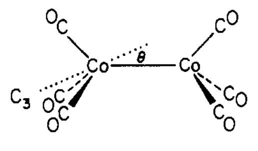
Figure 1. Molecular orbitals of the C_{2v} $(CO)_3Co-Co(CO)_3$ fragment.

The dimetal fragment orbitals are constructed as they were for $Fe_2(CO)_6$ by Thorn and Hoffmann, and the reader is referred to this article for a detailed development.[11] Two $Co(CO)_3$ fragments are brought together in D_{3h} symmetry to a Co–Co distance of 2.46 Å. The frontier orbitals of the $Co(CO)_3$ fragment[11,12] are shown in **8**. At low energy is the remnant of the octahedral t_{2g} set ($1a_1$ + 1e); at higher energy are the delocalized equivalents ($2a_1$ + 2e) of three hybrids pointing toward the vacant coordination sites.



8

The orbitals of D_{3h} $(CO)_3Co-Co(CO)_3$ are essentially the in- and out-of-phase combinations of the orbitals shown in **8**. Next, the cobalt tricarbonyl groups were bent back, maintaining local C_3 axes, **9**, to ready the $(CO)_3Co-Co(CO)_3$ for interaction with X_2. This bending reduces the symmetry of the entire fragment to C_{2v}. θ was taken to be 28°, as the geometry for this $Co_2(CO)_6$ fragment was idealized from that of the dimetal piece of $Co_2(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu_2)$. The important resulting orbitals are shown in Figure 1 with their C_{2v} sym-



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(7) (a) Campana, C. F.; Vizi-Orosz, A.; Palyi, G.; Marko, L.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3054–3059. (b) Foust, A. L.; Campana, C. F.; Sinclair, J. D.; Dahl, L. F. *Ibid.* **1979**, *18*, 3047–3054. Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633–5635.

(8) Using the isoelectronic μ-acetylene and μ-P_2 or μ-As_2 complexes as models for π-bonded dinitrogen adducts is not a novel idea. See for instance: Reference 7b. Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520–537; *Angew. Chem.* **1980**, *92*, 513–531. (b) For a fascinating alternative coordination mode of As_2 see: Sigwarth, B.; Zsolnai, L.; Berke, H.; Huttner, G. *J. Organomet. Chem.* **1982**, *226*, C5–C8.

(9) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

(10) A theoretical study of some members of this series has been published: Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103–3117. See also: Van Dam, H.; Lowen, J. N.; Oskam, A.; Doran, M.; Hillier, I. H. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 57–69.

(11) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126–140.

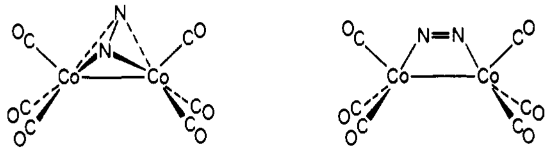
(12) Elian, M.; Hoffmann, R. *Ibid.* **1975**, *14*, 1058–1076. Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148–1154.

metry labels. The antisymmetric b_2 combination corresponding to the in-phase $4a_1$ orbital is too far up in energy to interact strongly with the X_2 fragment and is not shown in Figure 1. Of minor importance in the analysis to come will be the lower six orbitals pictured. These orbitals will contribute very little to the interaction picture of the dimetal fragment and the X_2 group. This is due to the poor overlap of these $Co(CO)_6$ orbitals with the X_2 orbitals and their involvement in significant back-bonding to the carbonyls.

The orbitals that we will be concerned with in this study are $3a_1$, $2b_1$, $2a_2$, $3b_2$, and $4a_1$ of Figure 1. These five orbitals are those that will interact most with the X_2 fragment.

$Co_2(CO)_6(\mu\text{-}N_2)$

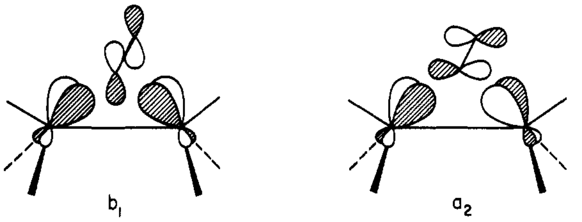
We consider two possibilities for the orientation of a bridging N_2 group π bonded to the dimetal fragment, $(CO)_3Co-Co(CO)_3$: **10a**, "perpendicular"; **10b**, "parallel".



a b

10

Shown in Figure 2 is the interaction diagram for the N_2 fragment and the $Co_2(CO)_6$ piece of complex **10a** at a Co–N distance of 2.0 Å. The N–N distance of 1.35 Å was taken from the known Jonas and Krüger structures.[2] Of immediate note is the significant degree of back-bonding. The empty b_1 and a_2 orbitals of N_2 overlap well with the filled $2b_1$ and $2a_2$ dimetal fragment orbitals, as shown schematically in **11**, and the difference in energy between the fragment orbitals is small as well. The extent of back-bonding may be seen from the occupation of the N_2 fragment π* orbitals in the composite molecule—b_1 is occupied by 1.07 electrons and a_2 by 1.01 electrons.



11

Of course, simultaneously the π orbitals are participating in forward donation. The ultimate effect of this forward and back donation process is necessarily to weaken the N–N bond. This is seen in the decrease in the overlap population of the N–N bond from free N_2 (of identical N–N distance) to the complexed N_2 of 1.27 to 0.87, respectively. The extent of the weakening may also be seen in the extreme bond lengthening that occurs in the two known side-on bonded N_2 structures.[2]

On the whole, the electronic structure of this complex appears to be quite reasonable. The bonding interactions are strong. There is a large HOMO–LUMO gap, a classical indicator of kinetic and thermodynamic stability. There is a 1.53– charge on the N_2 fragment, but this is just a consequence of the electronegativity difference between Co and N.

The parallel bonded geometry is very different. It has weaker interactions and a tiny 0.02-eV gap between filled and unfilled levels. Its energy is 3 eV above the perpendicular feature. For a detailed analysis of the similar problem in parallel vs. perpendicular acetylene bonding, the reader is referred to another study from our group.[9]

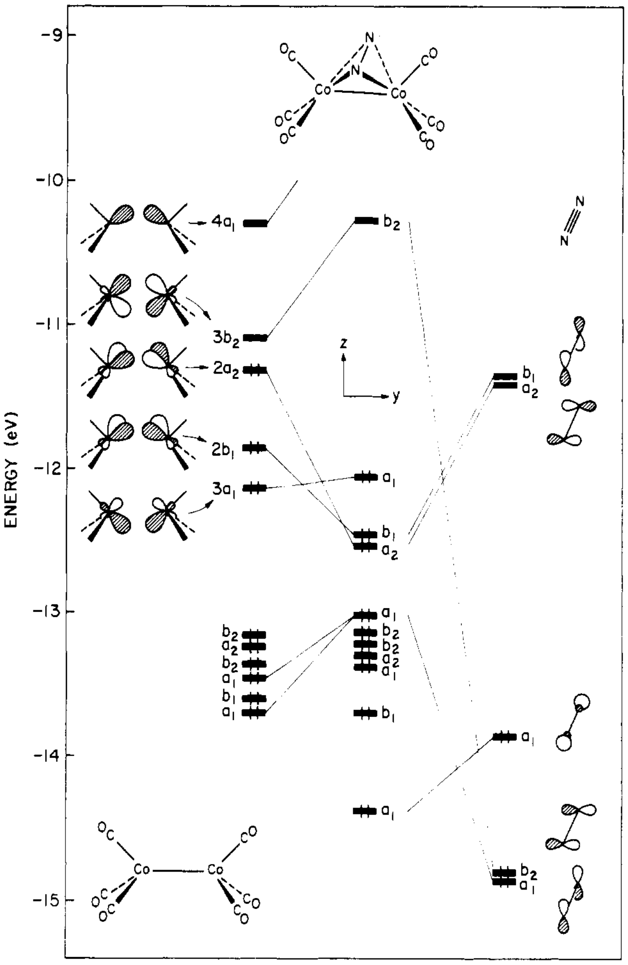
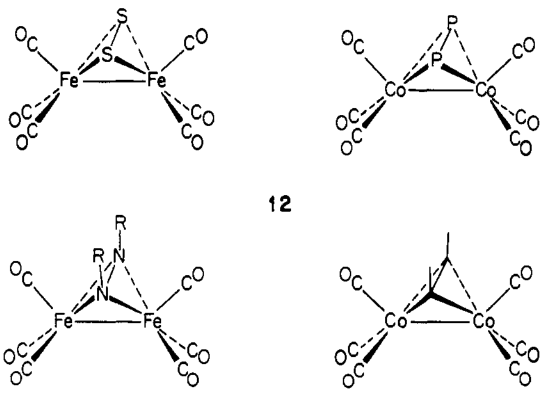


Figure 2. Interaction of $(CO)_3Co-Co(CO)_3$ with N_2 to form $(CO)_3Co(\mu\text{-}N_2)Co(CO)_3$. The bonding combinations of the N_2 π orbitals (a_1 and b_2) with the appropriate dimetal orbitals are low lying and are omitted from the center of the figure.

Comparison with Other $Co_2(CO)_6(\mu\text{-}X_2)$ Complexes

With the idea in mind that, if $Co_2(CO)_6(\mu\text{-}N_2)$ were to exist, its stable form would be that of a perpendicularly bridging (to the Co–Co axis) N_2 group, **10a**, let us examine some other complexes that are structurally and electronically similar, **12**.



12

Using the same dicobalt fragment previously developed,[13] we positioned various of the X_2 groups at a reasonable distance from the metals.[4–7] The interactions were then explored, with comparisons made to the missing member of the series, $Co_2(CO)_6(\mu\text{-}N_2)$.

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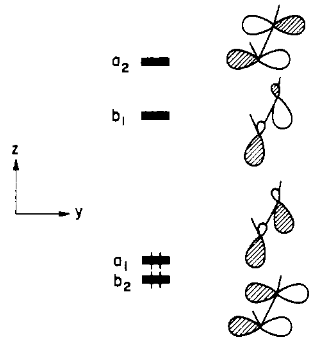
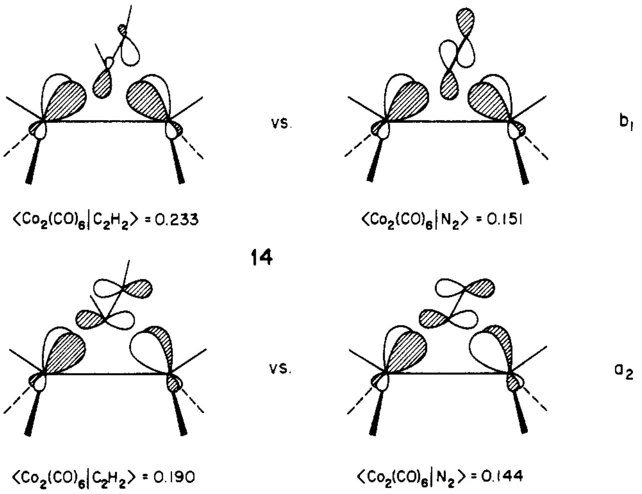
[13] With an appropriate charge for the known Fe_2 complexes.

Let us begin with the well-known acetylene structure. In the model system we choose for the calculation, the R groups are replaced by H atoms, and the geometry is idealized from $Co_2(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu_2)$.[4a] When acetylene complexes in this way, the R groups bend back, so that the RCC angle is between 130 and 150°. We made HCC 145° in our calculations. The degeneracy of the π and π^* orbitals is broken,[9] so that the resultant π and π^* levels appear as in **13**.



13

As we study the interaction diagrams for both the dinitrogen and acetylene complexes, Figures 2 and 3, we see that they are essentially the same picture. We have in the acetylene complex the same back-bonding previously noted for the N_2 species, where the empty b_1 and a_2 π^* orbitals interact with the filled metal orbitals, **14**.



14

These overlaps are substantially larger than the corresponding N_2 overlaps. Yet the magnitude of back-bonding is substantially higher for $Co_2(CO)_6(\mu\text{-}N_2)$. The π^* acetylene orbitals only reach occupations of 0.35 and 0.62 electron for a_2 and b_1, respectively, as compared to 1.01 and 1.07 electrons for the same orbitals of N_2. Employing the usual perturbation theoretic criteria, we can rationalize the more significant N_2 interactions by the better energy match between interacting orbitals. The differences in energy matches are great enough to compensate for the lesser overlap in the N_2 interactions.

There is, however, more forward donation in the acetylene complex with occupations of the π orbitals, a_1 and b_2 of 1.77 and 1.45 electrons, respectively. These are compared with the higher occupations of 1.88 and 1.70 electrons for the same orbitals in the N_2 fragment. But as in the N_2 complex, these forward and back donation processes act synergetically to weaken the C–C bond, and this result shows up in the overlap population as it falls from 1.69 in free C_2H_2 to 1.24 in complexed form.

If we look at the interaction diagrams of any of the other complexes in **12**, we find basically the same picture. There are, of course, minor differences in the strengths of the interactions due to slightly different energy levels and extensions in space of the X_2 frontier orbitals. So while we will refrain from presenting the interaction diagrams for the other complexes, we have compiled in Table I the X_2 fragment orbital occupations upon complexation, for purposes of comparison.

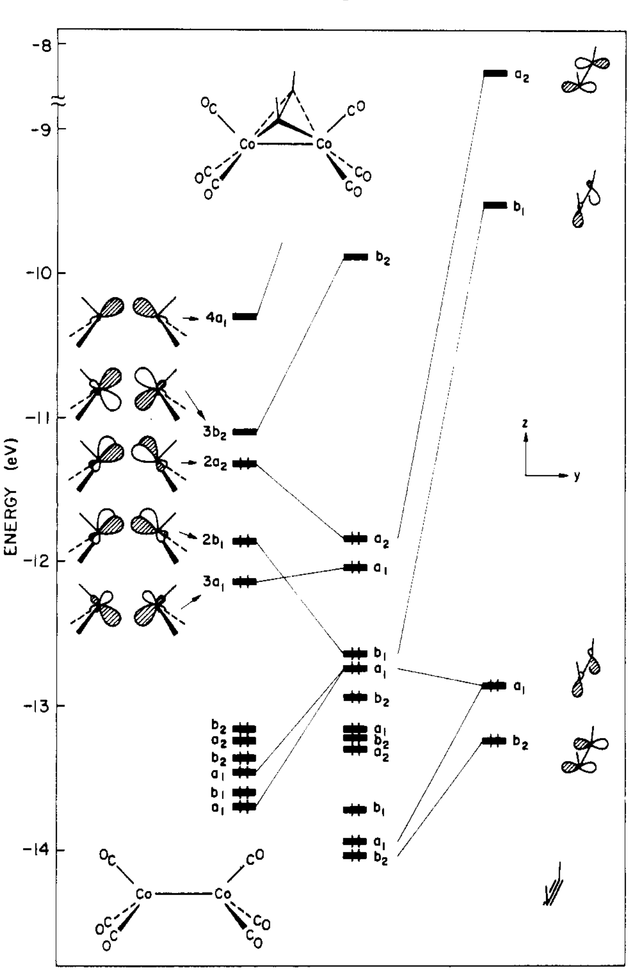


Figure 3. Orbital interaction diagram of acetylene with $(CO)_3Co$–$Co(CO)_3$.

Table I. Occupations of X_2 Fragment Orbitals

complex	orbital occupations, electrons					total charge on X_2
	π^*a_2	π^*b_1	a_1	πa_1	πb_2	
$Co_2(CO)_6(\mu\text{-}N_2)$	1.01	1.07	1.97	1.88	1.70	1.53–
$Co_2(CO)_6(\mu\text{-}P_2)$	0.94	1.00	2.00	1.81	1.65	1.28–
$Co_2(CO)_6(\mu\text{-}S_2)^{2+}$	1.05	1.09	2.00	1.81	1.59	0.61+
$Co_2(CO)_6(\mu\text{-}C_2H_2)$	0.35	0.62		1.77	1.45	0.13–
$Co_2(CO)_6(\mu\text{-}N_2H_2)^{2+}$	1.03	1.30		1.85	1.63	0.30+

All these complexes, be they bridged by N_2, P_2, S_2, HCCH, or HNNH, possess the same basic features. They have relatively large HOMO–LUMO gaps, substantial forward and back donations, and the inevitable weakening of the X–X bonds. All these complexes are similar in their electronic structure.

Known Structures

The electronic structure of the hypothetical $M_2L_6(\mu\text{-}N_2)$ complex appears reasonable. But how does it compare with the level scheme of the two known π-bonded dinitrogen complexes? If there are similarities in the unknown and established structures, we would gain confidence in our calculations of the hypothetical complex family.

As we mentioned in the introduction, the complicated Jonas structures may be simplified by (conceptual) removal of Na^+, Li^+, PhLi, and ether groups to a central and irreducible d^{10}–d^{10} $Ni_2Ph_4(\mu\text{-}N_2)^{4-}$ core. We carried out calculations on the phenyl complex and a simpler model with the phenyl groups

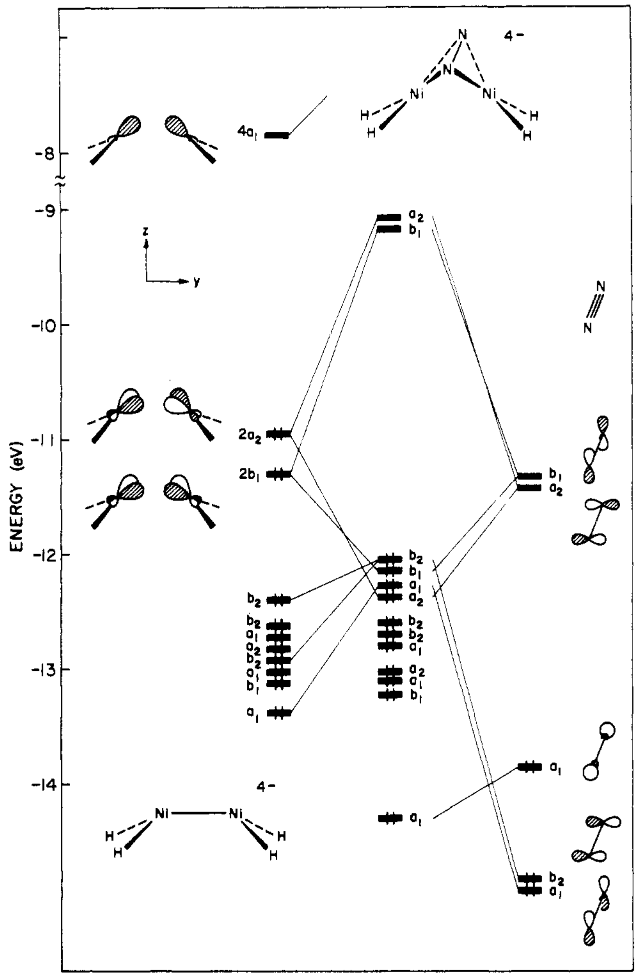
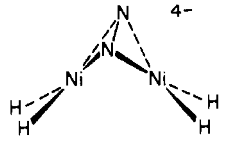


Figure 4. Molecular orbitals of the model system $H_2Ni(\mu\text{-}N_2)NiH_2^{4-}$, formed from the fragments $H_2NiNiH_2^{4-}$ and N_2. The bonding combinations of the N_2 π orbitals (a_1 and b_2) with the appropriate dimetal orbitals are low lying and are omitted from the center of the figure.

replaced by hydrides. This substitution has little effect on the interactions we will be concerned with, so in the subsequent discussion we will discuss only the $Ni_2H_4N_2^{4-}$ model, **15**.



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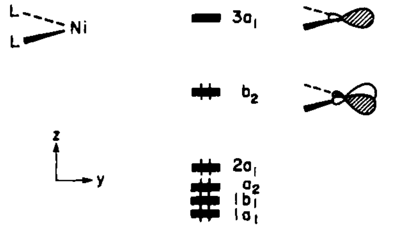
Each ML_2 fragment contributes the orbtials shown in **16**.[14]



16

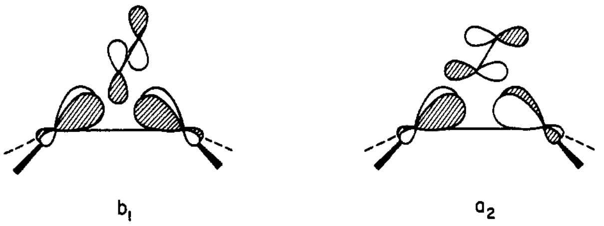
The L_2MML_2 orbitals are essentially the symmetric and antisymmetric combinations of these ML_2 fragment levels and are shown at the left in Figure 4. The lower eight orbitals do not interact strongly with the μ-N_2 fragment, which is at the right.

Table II. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
Co 3d	−13.18	5.55	2.10	0.5680	0.6060
4s	−9.21	2.0			
4p	−5.29	2.0			
Ni 3d	−12.99	5.79	2.0	0.5683	0.6292
4s	−8.86	2.10			
4p	−4.90	2.10			
P 3s	−18.6	1.60			
3p	−14.0	1.60			
S 3s	−20.0	1.817			
3p	−13.3	1.817			

[a] Coefficients in double-ζ expansion.

Of major concern to us will be the $2a_2$ and $2b_1$ orbitals, which look very similar to the two we have been concentrating on in the $Co_2(CO)_6$ study. Their interaction is also very familiar. The same back-bonding is recognized here, **17**. By



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the π* occupations of 1.24 and 1.12 electrons, one can see that the back donation is even greater in this known N_2 structure. This is due to the better overlap of the M_2L_4 fragment orbitals with respect to that of the M_2L_6 orbitals and is also noted for interactions in analogous acetylene complexes.[9] The forward donation is slightly less than that in the $Co_2(CO)_6(\mu\text{-}N_2)$ case, with π occupations falling to 1.89 and 1.81 electrons in the complex. The N–N bond is obviously weakened in this process, and the decrease in the overlap population (from 1.27 in free N_2 of the same bond distance to 0.84 in its complexed form) is only about 2% greater than the decrease noted for the Co_2 complex. There is a large gap between filled and unfilled orbitals.

On the whole, it seems that the interaction pictures for these two N_2 complexes, one hypothetical and the other tangible, are essentially superimposable, making exceptions, of course, for the obvious constraints of the different metal coordinations.

Existence of π-Bonded $L_nM(\mu\text{-}N_2)ML_n$ Structures

We are forced to conclude that there is nothing wrong with these bridging dinitrogen dinuclear transition-metal complexes. These compounds are predicted to be stable species. The calculations on the so far unobserved $Co_2(CO)_6(\mu\text{-}N_2)$ complex show it to resemble in every possible way known N_2 π-bonded complexes and the members of the isoelectronic series of $M_2L_6(\mu\text{-}X_2)$ presented earlier. Thus, the absence of this structure is most conspicuous. We eagerly await its synthesis.

Acknowledgment. We are grateful to the National Science Foundation for its support of the Undergraduate Research Program at Cornell University, which made K.I.G.'s stay at Cornell possible. We also thank J. Jorgensen for the drawings and E. Stolz for the typing.

Appendix

All calculations were performed by using the extended Hückel method,[15] with weighted H_{ij}'s.[16] The following bond

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(14) For the orbitals of ML_2 see: Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812. Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613. Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602–610. Hoffmann, P. *Angew. Chem.* **1977**, *89*, 551–553.

distances and angles were used in our calculations: N-N-($Co_2(CO)_6(\mu\text{-}N_2)$ and $Ni_2Ph_4(\mu\text{-}N_2)^{4-}$), 1.35 Å; Co-C, 1.8 Å; C-O, 1.16 Å; Co-Co, 2.46 Å; Co-N, 2.0 Å; P-P, 2.019 Å; Co-P, 2.264 Å; S-S, 2.007 Å; Co-S, 2.228 Å; C-C, 1.335 Å; Co-C, 1.996 Å; N-N($Co_2(CO)_6(\mu\text{-}N_2H_2)^{2+}$), 1.37 Å; Co-N, 1.878 Å; CO-Co-CO, 90°; Co-C-O, 180°; C-C-H, 145°; N-N-H, 123°.

Parameters for H, C, N, and O are the standard ones.[15] The parameters for P, S, Co, and Ni are from our previous work[11,14] and are compiled in Table II.

Registry No. $Co_2(CO)_6(\mu\text{-}N_2)$, 82838-96-8; $Co_2(CO)_6(\mu\text{-}P_2)$, 51244-37-2; $Co_2(CO)_6(\mu\text{-}S_2)^{2+}$, 82838-97-9; $Co_2(CO)_6(\mu\text{-}C_2H_2)$, 12264-05-0; $Co_2(CO)_6(\mu\text{-}N_2H_2)^{2+}$, 82838-98-0; $Ni_2Ph_2(\mu\text{-}N_2)^{4-}$, 82838-99-1.

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Contribution from the Istituto Chimica Generale, Facoltà di Farmacia, University of Florence,
and ISSECC, CNR, Florence, Italy

Exchange Interactions in Heterodinuclear Complexes with One Ion Possessing an Orbitally Degenerate Ground State. Nickel(II)-Cobalt(II) Pairs in Diaquo(1,4-dihydrazinophthalazine)nickel(II) Chloride Hydrate

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Received January 12, 1982

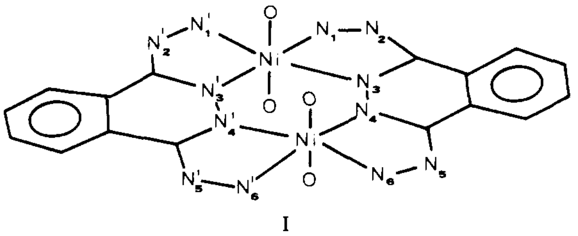
The EPR spectra of copper(II)- and cobalt(II)-doped diaquo(1,4-dihydrazinophthalazine)nickel(II) chloride hydrate, $Ni_2(dhph)_2(H_2O)_4Cl_4{\cdot}2H_2O$, have been recorded at liquid-helium temperature. Signals attributable to Ni-Co and Ni-Cu pairs were found and assigned on the basis of the hyperfine splitting patterns. In both cases the spectra could be interpreted within a $S = {}^1/_2$ spin Hamiltonian yielding the following: Ni-Cu, $g_1 = 2.07$, $g_2 = 2.21$, $g_3 = 2.25$; Ni-Co, $g_1 = 0.60$, $g_2 = 0.93$, $g_3 = 2.09$. The temperature dependence of the signal intensity of the Ni-Cu pairs shows that the coupling between the two metal ions is antiferromagnetic, as expected for two octahedra sharing an edge. For the Ni-Co pairs, in which the cobalt ion has an orbitally degenerate ground level, a simple model was used to calculate the exchange coupling constants of the nickel $^3A_{2g}$ ground level with the three orbital components of cobalt $^4T_{1g}$. The calculated parameters correspond in any case to antiferromagnetic interactions, the three exchange pathways being esstentially identical with each other.

Introduction

Exchange interactions in homo- and heterodinuclear transition-metal complexes are currently much studied,[1-5] and several theoretical models have been used with some success to correlate the observed coupling constants with the electronic structure of the individual ions.[6-8] The main limitation in the theoretical background is that only orbitally nondegenerate ground states can be easily handled. Introducing ground-state orbital degeneracy complicates enormously the patterns of interactions between the two metal ions, and the energy levels of the pairs can be expressed only by using a large number of parameters.[9] Some cases exist where the treatment has been performed by using models of different sophistication,[10-13] but as yet no definite trend starts to be apparent for the exchange interaction between orbitally degenerate ground states.

A simpler case, which in principle can be handled in a more tractable manner, is that relative to the interaction of an orbitally nondegenerate ion with an orbitally degenerate one.[14,15] In this case some simple models have been suggested, which have been applied to few experimental cases. In order to check their validity, however, it is necessary to study many more experimental data, trying to correlate the values of the parameters to the electronic structures of the complexes.

Cobalt(II) in an octahedral ligand field has a ground $^4T_{1g}$ level. Several dinuclear complexes have been reported in which octahedral cobalt(II) ions are present. An interesting series, for which crystal structure determinations are available, is that of diaquo(1,4-dihydrazinophthalazine)metal(II) chloride hydrate, $M_2(dhph)_2(H_2O)_4Cl_4{\cdot}2H_2O$, where metal can be either cobalt or nickel.[16-18] Structure I shows the complex with



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