

Molecular Nitrogen as a Ligand. A Study of Dinitrogen Complexes of Transition Metals, Diazocompounds, and Azides By X-ray Photoelectron Spectroscopy

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Received January 8, 1973

X-ray photoelectron $Ir4f_{7/2}$ -spectra of iridium(I) complexes with N_2 , CO and other ligands as well as N1s-spectra of Ir^I , Co^I , Fe^{II} dinitrogen complexes and of some diazocompounds and azides were studied. Donor-acceptor properties of dinitrogen ligand, character of its coordination and electron density distribution over nitrogen atoms were investigated. Dinitrogen ligand was shown to be in overall the electron acceptor, it being more effective than Ph_3P , CS and diphenylacetylene, close to CO and less effective than tetracyanoethylene. Dinitrogen fragment in organic diazocompounds bears the positive charge, while in transition metal complexes one of the nitrogen atoms was found to be negative charged. This results in the different reactivity of the compounds.

Introduction

A great number of molecular nitrogen complexes with transition metal compounds is known up-to-date.¹ The coordinated N_2 molecule in these complexes may be considered as a model of activated dinitrogen in the processes of its enzymatic and chemical fixation to ammonia. However, dinitrogen ligand in most known dinitrogen complexes, and first of all in mononuclear ones, still failed to be reduced even under the action of very strong reducing agents.

This fact is surprising, keeping in mind the certain similarity of mononuclear dinitrogen complexes of transition metals to aromatic and aliphatic diazocompounds and other molecules having diazogroup (azides, nitrous oxide). Actually, all these compounds are characterised by the same linear structure $A \equiv N \equiv N$ (where A - transition metal atom, C, N, O), as well as by similar NN-bond lengths (1.10-1.16 Å) and values $\nu_{N \equiv N}$ in IR spectra (1900-2300 cm^{-1}). It enables the dinitrogen complexes to be considered as some peculiar inorganic analoga of diazocompounds. From the chemical point of view, however, this analogy is to a great extent formal because diazogroup of real diazocompounds in most cases can be easily reduced.

To clear up the reasons of such a discrepancy and to compare the donor-acceptor properties of dinitrogen ligand in transition metal complexes with those of other neutral ligands we have used the X-ray photoelectron spectroscopy technique. This method enables the binding energy (E_{bind}) of atoms core electrons in a molecule to be determined.² The value of E_{bind} increases with decrease of electron density on the atom and *vice versa*, or more correctly is a function of potential in the region of the atom nucleus.³

The first investigation of Re^I dinitrogen complexes was performed by Leigh *et al.*⁴ and terminal nitrogen atom was shown to be negative charged.

Here we wish to report the results of X-ray photoelectron spectroscopy investigation of Ir^I , Co^I , Fe^{II} dinitrogen complexes and some diazocompounds and azides as well as of isostructural Ir^I complexes with N_2 , CO and other ligands.

Experimental Section

Spectra were recorded in Varian IEE-15 spectrometer and were excited by $AlK\alpha_{1,2}$ -radiation. X-ray tube operating conditions were 8 kV \times 80 mA. Vacuum - 10^{-6} torr. Intensity was registered each 0.09 eV. In most cases kinetic energy of electrons entering the β -spectrometer (E_{anal}) was equal to 100 eV which provided the maximum intensity. The mean accuracy and reproducibility of the data was about ± 0.1 eV. For each compound spectra were taken using two or more samples, prepared separately. The samples were prepared by application of fine powdered compounds to a thin organic film or by rubbing in a nickel net. When necessary this procedure was performed in a special chamber in the stream of dry cool dinitrogen. Some substances, in particular diazocompounds, decompose under X-ray radiation at room temperature. In such cases samples were cooled to -50 to $-100^\circ C$ in the spectrometer when taking the spectra.

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Table I. Reproducibility of binding energy values with charging effect taken into account.

No.	Compound	E_{bind}	C1s measured	Ir4f _{7/2} measured	Ir4f _{7/2} corrected
1.	(Ph ₃ P) ₂ Ir(CO)Cl		282.0 _s	58.6	61.5 _s
2.	(Ph ₃ P) ₂ Ir(CO)Cl		280.9 _s	57.5 _s	61.6
3.	(Ph ₃ P) ₂ Ir(CO)Cl		283.9	60.5 _s	61.6 _s
4.	(Ph ₃ P) ₂ Ir(CO)Cl		283.7 _s	60.2 _s	61.5
1.	(Ph ₃ P) ₂ Ir(N ₂)Cl		283.9	60.8 _s	61.9 _s
2.	(Ph ₃ P) ₂ Ir(N ₂)Cl		283.9 _s	60.8	61.8 _s
3.	(Ph ₃ P) ₂ Ir(N ₂)Cl		283.8 _s	60.6	61.7 _s
4.	(Ph ₃ P) ₂ Ir(N ₂)Cl		283.1	59.8	61.7

Since the accumulation of electrostatic charge on the sample cause change of measured values of E_{bind} , the C1s-line of phenyl group was used as an inner reference, its energy assumed to be 285,0 eV. The charging effect is inconstant and reach a few eV. For example, for each compounds (Ph₃P)₂Ir(CO)Cl and (Ph₃P)₂Ir(N₂)Cl four spectra were taken, the period between measurements 1,2 and 3,4 being a few months (see Table I, where presented are the measured C1s and Ir4f_{7/2} values of these compounds together with the Ir4f_{7/2} values corrected to the charging effect).

Thus, correction to the charging effect being taken into account, good reproducibility of resulting values was obtained.

Results and Discussion

1. *Ir4f_{7/2}-spectra.* Donor-acceptor properties of nitrogen molecule in complexes are being intensively studied by IR, Mössbauer spectroscopy and other methods. It seemed interesting to investigate the influence of dinitrogen ligand upon the effective charge of central atom in complex to compare with that of CO, Ph₃P and other ligands. With this in mind the X-ray photoelectron spectra of a series of isostructural *trans*-(Ph₃P)₂Ir(L)Cl complexes, where L = N₂, CO, CS, Ph₃P, PhC≡CPh, (CN)₂C=C(CN)₂ were studied. Complexes were obtained according to the procedures described in.⁵⁻⁸ Data on Ir4f_{7/2}-electrons spectra of the compounds investigated are summarized in Table II.

Since the binding energy should increase with the decrease of electron density on Ir, it follows from the data above that in the series of the compounds studied dinitrogen ligand is more strong electron acceptor than Ph₃P, CS, and PhC≡CPh and less strong one than tetracyanoethylene. The acceptor capacity of N₂ ligand is not less than that of CO or slightly exceed it.

It is of interest that (Ph₃P)₂Ir(N₂)Cl was shown by Collman *et al.*⁵ to escape the oxidizing addition reaction with H₂ unlike (Ph₃P)₂Ir(CO)Cl. This is in agreement with the fact that the reaction rate of H₂ with square Ir complexes decrease with the electron density on the central atom.⁹

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Table II. Binding energies of Ir4f_{7/2}-electrons (eV).

No.	Compound	Ir4f _{7/2}
1.	(Ph ₃ P) ₂ IrCl	60.6
2.	(Ph ₃ P) ₂ Ir(CS)Cl	61.2
3.	(Ph ₃ P) ₂ Ir(PhC≡CPh)Cl	61.4
4.	(Ph ₃ P) ₂ Ir(CO)Cl	61.6
5.	(Ph ₃ P) ₂ Ir(N ₂)Cl	61.8
6.	(Ph ₃ P) ₂ Ir[(CN) ₂ C=C(CN) ₂]Cl	62.7

Electron density on the transition metal atom in complexes is generally ascribed by the competition of σ -donor and π^* -acceptor interactions between ligand and metal. The first leads to increase of the electron density on metal, the latter favours its decrease. The X-ray photoelectron spectroscopy does not permit the contribution of each of these effects to be determined separately, but in the most interesting cases of N₂ and CO it is possible to correlate our results with the data on the relative π -acceptor and σ -donor capacity of these ligands obtained by other methods.

It has been shown¹⁰⁻¹⁴ that molecular nitrogen is both the weaker σ -donor and the weaker π -acceptor than carbon monoxide. On the other hand CO ligand is usually considered to be totally an electron acceptor, i.e. in this case the π^* -acceptor interaction makes the greater contribution to the binding with metal than the σ -donor one. That fact that N₂ according to our data is slightly stronger acceptor (in overall) than CO, may indicate that the contribution of d- π^* -interaction to the formation of M-N₂ bond is probably still greater than to M-CO bond formation.

It should be noted that comparison of the total donor-acceptor ability of N₂ with that of CO, drawn by different methods for various compounds gives diverse results.

Thus Sellman¹⁵⁻¹⁷ has detected in H¹-NMR spectra of complexes C₅H₅Mn(CO)₂L, C₅H₅Re(CO)₂L, and C₆H₆Cr(CO)₂L (L = N₂) an aromatic ring protons shift of 3-12 Hz to a stronger field in comparison with those of complexes where L = CO. He came

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to a conclusion that N₂ is so or less effective electron acceptor than CO.

On the other hand, having analysed the Mössbauer spectra of cationic complexes [FeH(L)(Et₂PCH₂CH₂PEt₂)₂]BF₄ where L = N₂ or CO, Bancroft *et al.*¹⁸ showed that N₂ is poorer (π+σ) ligand, but better (π-σ) one. These results indicate that in this case π-acceptance relative to σ-donation is more important in N₂ complex than in CO one.

It is of interest that the better acceptor capacity of N₂ in comparison with CO manifests itself also in some compounds having these groups covalent bonded with other atoms. For example it is evidenced by the data on X-ray photoelectron spectra of [NNN]⁻ and [OCN]⁻ ions,¹⁹ which may be considered as "complexes" of N₂ and CO with N⁻.²⁰ The N1s-electrons binding energies of the terminal nitrogen atom in these compounds are equal to 399.3 eV and 398.3 eV respectively, i.e. the electron density on this nitrogen atom is less in the first case. Similar data have been obtained also for N₂O and CO₂.²¹ The O1s-electrons binding energy for O=N=N is equal to 541.2 eV and for O=C=O to 540.8 eV.

Thereafter it should be admitted that donor-acceptor properties of N₂ and CO may depend on the nature of central atom and surrounding ligands.

2. N1s-spectra. The N1s-spectra analysis permit a conclusion to be drawn about the influence of coordination on the electron density distribution over nitrogen atoms in dinitrogen complexes and about the character of dinitrogen coordination with central atom.

Thus in a spectrum of (Ph₃P)₂Ir(N₂)Cl a very wide N1s line with slight splitting into two components is observed. It can be considered as a superposition of two peaks at 399.9 eV and 401.5 eV.

(Ph₃P)₃Co(N₂)H complex (prepared according²²) gives a wide N1s line with a maximum at 400.1 eV and 3.3 eV half-width. (Ph₃P)₃Fe(N₂)H₂ (prepared according²³) gives a line with a maximum at 400.2 eV and 3.2 eV half-width. Analysis of the wide spectral band gives the N1s values for (Ph₃P)₃Co(N₂)H equal to 399.4 eV and 400.8 eV and for (Ph₃P)₃Fe(N₂)H₂ equal to 399.5 eV and 400.9 eV.

The data demonstrate the nonequivalence of N-atoms in these complexes which agrees with the dinitrogen linear coordination of M≡N≡N type. It should be pointed out that while for (Ph₃P)₃Co(N₂)H there is the direct X-ray diffraction evidence of M-N₂ fragment linearity,²⁴ for (Ph₃P)₂Ir(N₂)Cl and (Ph₃P)₃Fe(N₂)H₂ the N₂ coordination is considered linear on the basis of indirect data on integral intensity measurements of ν_{N≡N} band in IR spectra.¹¹ Thus, the X-ray photoelectron spectroscopy data are the convincing evidence of such a conclusion.

N1s-spectra of different diazonium salts, diphenyldiazomethane, p-quinondiazide and β-naphthylazide were taken to be compared with those of dinitrogen complexes. All these compounds had been obtained solid according to the known procedures just before taking their spectra. Diphenyldiazomethane and β-naphthylazide show in the spectra two resolved peaks. Other diazocompounds investigated show a broad line with half-width of 3.2-3.6 eV. The resolution of this line in two components allows the N1s values with an accuracy of ±0.2 eV to be estimated.

Additionally the N1s-spectrum of sodium azide was taken. Our results for NaN₃ as well as for PhN₂BF₄ are in good agreement with the literature data.^{2,19,25}

N1s-lines maxima in spectra of Ir^I, Co^I, and Fe^{II} dinitrogen complexes, diazocompounds and azides as well as values of ν_{N≡N} in IR spectra of these compounds are given in Table III together with the literature data on Re^{4,26,27} and Ru²⁵ dinitrogen complexes.

From data in Table III it follows that the specific feature of the dinitrogen complexes under consideration, which distinguishes them from aromatic and aliphatic diazocompounds and azides, is the higher electron density on the dinitrogen fragment.

It should be noted that NN bond stretching vibration frequency in these compounds tends to decrease

Table III. N1s-electrons binding energies and NN bond vibration frequencies of dinitrogen complexes, diazocompounds and azides.

No. Compound	E _{N1s} (eV)	ν _{N≡N} (cm ⁻¹)
1. (Me ₂ PhP) ₂ Re(N ₂)Cl ^a	398.4	400.1 1922
2. (MePh ₂ P) ₂ Re(N ₂)Cl ^b	398.5	400.1 1939
3. (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ Re(N ₂)Cl ^a	398.8	400.9 1980
4. [(Me ₂ PhP) ₂ Re(N ₂)Cl]FeCl ^c	400.1	2000
5. [(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ Re(N ₂)Cl]FeCl ^c	400.3	2060
6. (Ph ₃ P) ₃ Co(N ₂)H	399.4	400.8 2088
7. (Ph ₃ P) ₃ Fe(N ₂)H ₂	399.5	400.9 2074
8. (Ph ₃ P) ₂ Ir(N ₂)Cl	399.9	401.5 2105
9. [(diars) ₂ Ru(N ₂)Cl]PF ₆ ^d	400.7	402.3 2130
10. Ph ₂ CN ₂	400.8	402.9 2050
11. p-OC ₆ H ₄ N ₂	401.5	402.9 2110
12. NaN ₃ ^e	399.3	403.7 2140
13. β-C ₁₀ H ₇ N ₃ ^e	401.3	404.4 2115
14. p-HOC ₆ H ₄ N ₂ HSO ₃	402.7	404.2 2235
15. p-CH ₃ OC ₆ H ₄ N ₂ HSO ₃	403.0	404.5 2255
16. m-SO ₂ C ₆ H ₄ N ₂	403.5	404.9 2280
17. p-SO ₂ C ₆ H ₄ N ₂	403.5	404.9 2285
18. PhN ₂ HSO ₃	403.7	404.9 2294
19. PhN ₂ BF ₄	403.7	404.9 2296
20. PhN ₂ BF ₄ ^f	403.8	405.1 2296

^a Data from ref. 26. ^b Data from ref. 27. ^c Data from ref. 26. Broad line with 3.5 eV half-width. It is considered⁴ as an unresolved doublet with components separated by about 1 eV, but the exact values of these components have not been calculated. ^d Data from ref. 25. Formula (diars)₂Ru(N₂)Cl, which is printed in²⁵, is not correct (see ref. 28). Diars = o-phenylenebis(dimethylarsine). ^e The ratio of two peaks intensity is 2:1. ^f Data from ref. 25.

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with increasing of electron density on N_2 fragment. It points to the increase of $d-\pi^*$ -interaction participation in NN bond loosening.

Unfortunately the X-ray photoelectron spectroscopy permit neither the atom effective charge nor even its sign from E_{bind} value to be estimated precisely. It is a consequence of the different accuracy of charge calculation by different methods and the relative character of the effective charge determination itself. Nevertheless with the limited accuracy such a correlation between E_{bind} and atom charge can be performed. Thus Siegbahn *et al.*² correlated the N1s values of numerous compounds with nitrogen atoms charges in these compounds, calculated by Pauling method. Hendrickson *et al.*¹⁹ made use of charges calculated by extended Hückel and CNDO methods. The slope of the correlation line and the position of the neutral nitrogen atom depend on the method of calculation. The range of N1s values for neutral nitrogen atom lays according to these calculations between 399-401 eV. It should be noted however that N1s binding energy of negativ charged terminal atoms in N_3^- anion is equal to 399.3 eV.

It may be concluded from the data in Table III that in organic diazocompounds nitrogen atoms bear positive charge while in most of dinitrogen complexes at least one of nitrogen atoms is negative charged.

Of course, it is to be taken in account that electron density on the dinitrogen fragment in complexes must depend on nature and oxidation state of central atom

and on surrounding ligands. Actually, the N1s values of Ru^{II} cationic dinitrogen complex trend to those of diazocompounds. On the whole, however, for complexes of molecular nitrogen more typical seems to be the negative charge, at least on one of nitrogen atoms.

Thus the molecular nitrogen complexes on one hand and diazocompounds and azides on the other differ in electron density distribution on nitrogen atoms which is probably one of the reasons of their different chemical reactivity. Unlike the diazocompounds, an attack of reducing agents, such as H^- and R^- , to the dinitrogen ligand of transition metal complexes should be hindered and directed to the metal. This may result in dinitrogen ligand displacement out of the coordination sphere.

More preferable for the dinitrogen ligand in complexes should be the reactions with electrophilic agents. This conclusion is in agreement with very interesting findings of Chatt *et al.*²⁹⁻³² that in some dinitrogen mononuclear Re^I , Mo^0 , W^0 , and Os^{II} complexes dinitrogen ligand displays basic properties, Lewis and protic acids added to the terminal nitrogen atom.

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