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Molybdenum—Nitrogen Bond-Strength Bond-Length Relationships

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Abstract

Parameter values (d_1,N) of (1·950, 5·75) for Mo^{VI}—N and (1·893, 5·1) for Mo^{V}—N bonds have been determined empirically for use in the general bond-strength (s) bond-distance (d) relationship $s = (d/d_1)^{-N}$ on the basis of structural data taken from 30 independent all-nitrogen and mixed (N,O) molybdenum coordination spheres in 21 different compounds.

Introduction

Molybdenum compounds have recently attracted considerable attention because of the interest in the chemistry of the earlier transition metals and their biological (Stiefel, 1977) and industrial (Braithwaite, 1978) importance. Molybdenum appears as an essential element in a number of enzyme processes, including that of symbionic nitrogen fixation, and its compounds are in wide use as catalysts.

It is well known that molybdenum tends to act as a typical π acceptor and exhibits a characteristic affinity towards oxygen, sulphur and the halogens, but less towards nitrogen. In the high-valence states, a common type of adduct therefore involves molybdenum in a basically octahedral environment with typically two terminal oxygens. As π donation from oxo ligands to the metal occurs less readily at lower formal oxidation states, only a few poorly characterized oxo species of $Mo^{IV,III}$ are known (Bart & Ragaini, 1979). Low-valent molybdenum chemistry is thus not heavily dominated by the oxo grouping. In considering the chemistry of molybdenum with simple nitrogen ligands, account should be taken of the fact that the cation exhibits a wide range of oxidation states and stereogeometries. Typically, in the tetravalent state the range of coordination numbers (4–8) involving nonoxo ligands is greater than for any other oxidation state.

In the interpretation and use of structural results, especially in case of irregular stereogeometries, advantage should be taken of bond-strength (s) bond-length (d) criteria. This avoids the use of individual radii and obviates the need for assumptions regarding the nature of the chemical binding. A knowledge of bond strengths facilitates the interpretation of spectral data. It appears that parameter sets for s–d relations are largely confined to bonds to oxygen (Brown & Wu, 1976), although a few others have been suggested (Brown, 1974; Hoggins & Steinfink, 1976; Zachariasen, 1978), but none for nitrogen. Therefore, this note evaluates Mo—N bond strengths on the basis of structural data (Table 1) for molybdenum complexes with all-nitrogen and mixed (N,O) ligand sets for which structural data are available.

Results and discussion

Analytical bond-strength bond-length relations are usually taken to conform to inverse power or logarithmic functions (Donnay & Allmann, 1970; Pyatenko, 1972; Brown & Shannon, 1973; Allmann, 1975; Brown & Wu, 1976). These expressions are essentially equivalent over the range of interest, with some deviations for bond strengths lower than about 0·2 v.u. Consequently, the procedure adopted here consists of describing the non-linear relation as $s = (d/d_1)^{-N}$, where d_1 and N are fitted values such as to ensure that the cation valence is obtained by summation of s over all the bonds to molybdenum. The expression $s = (d/1{\cdot}882)^{-6{\cdot}0}$ has recently been shown to describe adequately Mo—O bonding for the range of molybdenum valence states from 2+ to 6+ (Bart & Ragaini, 1979).

According to Table 1, few all-nitrogen ligand sets have appeared in molybdenum coordination compounds. Structural data for $[Mo_2(Me_2N)_6]$ and $[Mo(Me_2N)_4]$ indicate an effect of the molybdenum valence state on the Mo—N bond length. Consequently, various

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Table 1. *Bond strengths and bond lengths in molybdenum–oxygen and –nitrogen coordination spheres*

Compound[a]	Bond distances (Å)			Formal Mo valence state	$\sum s_{\mathrm{Mo-O}}$[b,c]	$\sum s_{\mathrm{Mo-N}}$[c,d]	$\sum s$[c]	σ_d[e]	Structural unit	Reference
	Mo–O	Mo–N	Mo–Mo							
$[Mottp(O_2)_2]$	1·958 (4×)	2·096 (4×)	–	6·0	3·15	2·64	5·79 (4)	0·004	MoO_4N_4	*n*
$[Mo(py)\{(Me_2OP\}O(O_2)]$	1·658, 1·905, 1·918, 1·938, 1·943, 2·035	2·450	–	6·0	6·25	0·27	6·52 (10)	0·012	MoO_6N^f	*o*
$NH_4[Mo(uda)O_2].H_2O$	1·680, 1·689, 1·991, 2·024, 2·140	2·337	–	6·0	5·71	0·35	6·06 (5)	0·005	MoO_5N^g	*p*
$K_3[Mo(nta)O_3].H_2O$	1·735, 1·737 (2×), 2·176, 2·245	2·388	–	6·0	5·63	0·31	5·94 (3)	0·005	MoO_5N^g	*q*
$Na_4[Mo_2(edta)O_6].8H_2O$	1·731, 1·739, 1·749, 2·176, 2·213	2·399	–	6·0	5·61	0·30	5·91 (4)	0·006	MoO_5N^g	*r*
$[Mo(C_9H_6NO)_2O_2]$	1·71 (2×), 1·98 (2×)	2·32 (2×)	–	6·0	5·03	0·74	5·77 (40)	0·03	$MoO_4N_2^g$	*s*
$[Mo(saltn)O_2]$	1·701, 1·714, 1·939, 2·074	2·135, 2·313	–	6·0	4·98	0·97	5·95 (3)	0·004	$MoO_4N_2^g$	*t*
$[Mo(dien)O_3]$	1·735 (2×), 1·739	2·320 (2×), 2·332	–	6·0	4·86	1·09	5·95 (10)	0·008	$MoO_3N_3^g$	*u*
$H[Mo\{(OCH_2CH_2)_3N\}O_2]$	1·75, 1·80, 1·91, 1·94, 2·34	2·44	–	5·0	4·87	0·27	5·14 (22)	0·04	MoO_5N^g	*v*
	1·77, 1·83, 1·93, 1·97, 2·35	2·42	–	5·0	4·51	0·29	4·80 (22)	0·04		
$[Mo_2(C_{20}H_{20}N_4O_8P_2)]$	1·68, 1·94 (2×), 2·10	2·27, 2·33	2·553 (4)	5·0	4·16	0·74	4·90 (15)	0·02	$MoO_4N_2^g$	*w*
	1·68, 1·94 (2×), 2·10	2·24, 2·31	2·553 (4)	5·0	4·16	0·79	4·95 (15)	0·02		
$(pyH)_3[Mo_2(MeCO_2)(NCS)_4O_4]$	1·690, 1·933, 1·954, 2·277	⟨2·136 (2×)⟩	2·560 (1)	5·0	3·88	1·08	4·96 (4)	0·006	$MoO_4N_2^g$	*x*
	1·675, 1·931, 1·961, 2·335	⟨2·136 (2×)⟩	2·560 (1)	5·0	3·92	1·08	5·00 (4)	0·006		
$(pyH)_3[Mo_2(MeCO_2)(NCS)_4O_3]$	1·693, 1·932, 1·952, 2·277	2·119, 2·138	2·560 (1)	5·0	3·86	1·10	4·96 (5)	0·007	$MoO_4N_2^g$	*y*
	1·674, 1·934, 1·961, 2·336	2·130, 2·155	2·560 (1)	5·0	3·92	1·06	4·98 (5)	0·007		
$(pyH)_3[Mo_2(HCO_2)(NCS)_4O_4].2H_2O$	1·677, 1·928, 1·945, 2·317	2·119, 2·138	2·566 (1)	5·0	3·97	1·10	5·07 (6)	0·008	$MoO_4N_2^g$	*y*
	1·676, 1·930, 1·951, 2·336	2·122, 2·134	2·566 (1)	5·0	3·94	1·10	5·04 (6)	0·008		
$(pyH)_4[Mo_2(C_2O_4)_2(NCS)_4O_3]$	1·677, 1·851, 2·112, 2·197	2·073, 2·094	–	5·0	4·00	1·23	5·23 (4)	0·005	$MoO_4N_2^g$	*y*
$(pyH)_4[Mo_2(HCO_2)_2(NCS)_6O_3]$	1·666, 1·858, 2·115, 2·230	2·065, 2·081	–	5·0	4·02	1·26	5·28 (6)	0·005	$MoO_4N_2^g$	*y*
$[Mo_2(\text{L-histidine})_2O_4].3H_2O$	1·71, 1·92 (2×), 2·21	2·21, 2·24	2·552 (n.d.)	5·0	3·93	0·88	4·81 (13)	0·02	$MoO_4N_2^g$	*z*
$[Mo_2(C_{10}H_8N_2)_2(H_2O_2P)_2O_4]$	1·678, 1·924, 1·944, 2·080	2·258, 2·325	2·554 (3)	5·0	4·24	0·76	5·00 (9)	0·012	$MoO_4N_2^g$	*aa*
	1·682, 1·916, 1·949, 2·097	2·240, 2·316	2·554 (3)	5·0	4·19	0·78	4·97 (9)	0·012		
$(pyH)_4[Mo(NCS)_3O_2]_2$	1·62, 1·92, 2·01	2·09, 2·15, 2·28	2·582 (2)	5·0	4·02	1·51	5·53 (19)	0·02	$MoO_3N_3^g$	*bb*
	1·66, 1·90, 1·91	2·13, 2·14, 2·21	2·582 (2)	5·0	3·98	1·54	5·52 (16)	0·02		
$(pyH)_4[Mo(NCS)_3O_2]_2.H_2O$	1·646, 1·963, 1·964	2·135, 2·144, 2·260	2·581 (1)	5·0	3·79	1·48	5·27 (6)	0·007	$MoO_3N_3^g$	*y*
	1·644, 1·940, 1·945	2·139, 2·149, 2·242	2·581 (1)	5·0	3·90	1·48	5·38 (6)	0·007		
$[Mo_2(tpp)_2O_3]$	1·707, 1·936	2·090, 2·093, 2·097 (2×)	–	5·0	2·64	2·39	5·03 (2)	0·003	$MoO_2N_4^g$	*cc*
$[Mo(i\text{-}PrO)_3(NO)]_2$	1·850, 1·861, 1·951, 2·195	1·747	–	not	3·38	1·51	4·89 (4)	0·009	MoO_4N^h	*dd*
	1·849, 1·857, 1·946, 2·194	1·761	–	given	3·41	1·45	4·86 (4)	0·009		
$[Mo(Me_2N)_4]$	–	1·917, 1·921, 1·924, 1·932	–	4·0	–	4·0	4·00 (2)	0·005	MoN_4^i	*ee*
	–	1·927 (2×), 1·928, 1·934	–	4·0	–	4·0	4·00 (2)	0·005		
$K_4[Mo_4(edta)_2O_4(OH)_2].16·4H_2O$	1·899, 1·938, 2·087, 2·148, 2·160	2·291	2·410 (1)	3·5	3·21	n.d.	n.d.	0·005	MoO_5N^g	*ff*
	1·899, 1·929, 2·078, 2·146, 2·165	2·279	2·410 (1)	3·5	3·25	n.d.	n.d.	0·005		
$K[Mo_2(edta)(CH_3CO_2)(OH)_2]$	2·03, 2·05, 2·11, 2·13, 2·14	2·18	2·430 (3)	3·0	2·68	0·28	2·96 (4)	0·02	MoO_5N^g	*gg*
$[Mo_2(Me_3SiO)_6(Me_2HN)_2]$	1·925, 1·949, 1·976	2·285	2·242 (1)	3·0	2·43	n.d.	n.d.	0·005	$Mo_2O_6N_2$	*hh*
	1·926, 1·940, 1·981	2·278	2·242 (1)	3·0	2·44	n.d.	n.d.	0·005		
$[Mo_2(Me_2N)_6]$	–	⟨1·980⟩ (3×)	⟨2·214 (3)⟩	3·0	–	3·00	3·00 (2)	0·007	$Mo_2N_6^j$	*ii*
$K_3[Mo(NCS)_6].H_2O.CH_3COOH$	–	2·034, 2·065 (2×), 2·107, 2·119 (2×)	–	3·0	–	3·08	3·08 (4)	0·018	MoN_6^g	*jj*
$[Mo_2(CF_3CO_2)_4].2C_5H_5N$	2·098, 2·111, 2·125, 2·128	2·548	2·129 (2)	2·0	1·98	n.d.	n.d.	0·007	$Mo_2O_8^{k,l}$	*kk*
$[Mo_2\{Et_2(pz)_2B\}_2(CH_3CO_2)_2].CS_2$	2·116, 2·120	2·158, 2·172	2·129 (1)	2·0	0·98	n.d.	n.d.	0·005	$Mo_2O_4N_4^k$	*ll*
	2·099, 2·106	2·158, 2·161	2·129 (1)	2·0	1·03	n.d.	n.d.	0·005		
$[Mo_2\{(pz)_3HB\}_2(CH_3CO_2)_2]$	2·08, 2·13	2·13, 2·18	2·147 (3)	2·0	1·02	n.d.	n.d.	0·02	$Mo_2O_4N_4^{k,l}$	*ll*
	2·11, 2·13	2·16, 2·19, 2·45	2·147 (3)	2·0	0·98	n.d.	n.d.	0·02		
$[Mo_2\{PhC(NPh)_2\}_4]$	–	2·125, 2·149 (2×), 2·163	2·090 (1)	2·0	–	n.d.	n.d.	0·009	$Mo_2N_8^k$	*mm*
$[Mo_2(mhp)_4].CH_2Cl_2$	2·076, 2·093	2·143, 2·176	2·065 (1)	2·0	1·08	n.d.	n.d.	0·007	$Mo_2O_4N_4^k$	*nn*
	2·084, 2·092	2·171, 2·177	2·065 (1)	2·0	1·07	n.d.	n.d.	0·007		
$[MoW(Me_3CCO_2)_4]I,CH_3CN$	⟨2·081⟩ (4×)	2·71	2·194 (2)[m]	2·0	2·19	n.d.	n.d.	0·013	$MoWO_8NI$	*oo*

(*a*) Abbreviations: dien, diethylenetriamine; edta, ethylenediaminetetraacetate; Et, ethyl; mhp, 6-methylpyridine; nta, nitrilotriacetate; Me, methyl; Ph, phenyl; *i*-Pr, isopropyl; py, pyridine; pz, pyrazolyl; saltn, bis(salicylaldehyde)trimethylenediiminate; tpp, dianion of α,β,γ,δ-tetraphenylporphyrin; ttp, tetra-*p*-tolylporphine; uda, uramil-*N*,*N*-diacetate. (*b*) Calculated according to the equation $s_{\mathrm{Mo-O}} = (d_{\mathrm{Mo-O}}/1·882)^{-6·0}$. (*c*) In valence units. Standard deviations were estimated for the shortest *d* value of the set. (*d*) Calculated with the following parameter sets [d_1 and N of $s = (d/d_1)^{-N}$]: 1·950, 5·75 (VI); 1·893, 5·1 (V); 1·926, *N* (IV); 1·980, 13·4 (III). (*e*) In ångström units. (*f*) Pentagonal bipyramid. (*g*) Octahedron. (*h*) Trigonal bipyramid. (*i*) Tetrahedron. (*j*) The Mo_2^{4+} unit is coordinated at six sites. (*k*) The Mo_2^{4+} binuclear unit is coordinated at eight sites. These may be considered to be at the corners of eclipsed squares whose centres are occupied by the metal ions. (*l*) Disregarding the weak axial donor. (*m*) Heteronuclear molybdenum–tungsten bond. (*n*) Chevrier, Diebold & Weiss (1976). (*o*) Le Carpentier, Schlupp & Weiss (1972). (*p*) Butcher & Penfold (1976*a*). (*q*) Butcher & Penfold (1976*b*). (*r*) Park, Glick & Hoard (1969). (*s*) Atovmyan & Sokolova (1971). (*t*) Chiesi Villa, Coghi, Gaetani Manfredotti & Guastini (1974). (*u*) Cotton & Elder (1964). (*v*) Atovmyan & Krasochka (1970). (*w*) Gatehouse, Nunn, Guerchais & Kergoat (1976). (*x*) Głowiak, Sabat, Sabat & Rudolf (1975). (*y*) Jezowska-Trzebiatowska, Głowiak, Rudolf, Sabat & Sabat (1977). (*z*) Delbaere & Prout (1971). (*aa*) Gatehouse & Nunn (1976). (*bb*) Kamenar, Penavič & Korpar-Čolig (1978). (*cc*) Johnson & Scheidt (1978). (*dd*) Chisholm, Cotton, Extine & Kelly (1978). (*ee*) Chisholm, Cotton & Extine (1978). (*ff*) Sheldrick (1976). (*gg*) Kneale & Geddes (1975). (*hh*) Chisholm, Cotton, Extine & Reichert (1978). (*ii*) Chisholm, Cotton, Frenz, Reichert, Shive & Stults (1976). (*jj*) Knox & Eriks (1969). (*kk*) Cotton & Norman (1972). (*ll*) Collins, Cotton & Murillo (1976). (*mm*) Cotton, Inglis, Kilner & Webb (1975). (*nn*) Cotton, Fanwick, Niswander & Sekutowski (1978). (*oo*) Katović, Templeton, Hoxmeier & McCarley (1975).

(d_1,N) parameter sets are to be derived to describe Mo—N bonding. The following structural data may be used as a reference [compound, Mo oxidation state, bond length (Å), bond strength (v.u.)]: $[Mo(Me_2N)_4]$, (IV), 1·926 (6), 1·0; $[Mo_2(Me_2N)_6]$, (III), 1·980 (7), 1·0; $[Mo(NCS)_6]^{3-}$ anion, (III), 2·085 (18), 0·50; $[Mo_2\{PhC(NPh)_2\}_4]$, (II), 2·146 (9), 0·50. Similar data are not available for the higher-valency states and additional reference points can therefore be evaluated only indirectly, namely by subtraction of the oxygen contributions from the total molybdenum valence sum in complexes with (N,O) ligand sets. This generates the following data: $[Mo(dien)O_3]$, (VI), 2·324 (5), 0·38; $[Mo(ttp)(O_2)_2]$, (VI), 2·096 (4), 0·71; $[Mo_2(tpp)_2O_3]$, (V), 2·094 (3), 0·59; $(pyH)_3[Mo_2(MeCO_2)(NCS)_4O_4]$, (V), 2·136 (6), 0·55; $[Mo_2\{Et_2(pz)_2B\}_2(CH_3CO_2)_2].CS_2$, (II), 2·162 (5), 0·50. Obviously, the latter data set suffers from some undesired interdependency of the Mo—N bond strengths on the values which describe Mo—O bonding. Initially obtained (d_1,N) parameter sets were then adjusted by minimizing the discrepancies of the calculated bond-strength sums and formal valence states using all available structural data (Table 1). Parameter (d_1,N) values of (1·950, 5·75) and (1·893, 5·1) for Mo^{VI}—N and Mo^{V}—N bonds, respectively, result in calculated cation bond-valence sums in close agreement with the formal oxidation states. It is apparent that the present available data still allow for a considerable uncertainty in the parameter values as (1·970, 6·2) and (1·946, 6·7) for Mo^{VI}—N and Mo^{V}—N bonds, respectively, are also fairly adequate. Similar expressions for less frequently occurring valence states could not be derived, although the quoted reference values allow (1·980, 13·4) to be established for Mo^{III}—N bonds. However, it is felt that this set requires further support.

Detailed examination of the results shows an average deviation of the calculated cation valence sums from the ideal valence values in Table 1 of about 3·0%, although there are individual deviations of up to about 10% in some structures. These discrepancies are partly due to uncertainties in the bond-length values, as indicated in the table by errors given for the bond-strength sums. Although many interatomic distances are quoted with standard errors of 0·005 Å or less, it is well known that they are subject to systematic errors larger than this, as, for example, when the effect of thermal motion has not been corrected for. The true standard errors are therefore much larger than the values quoted. This obviously would improve the agreement between the bond-strength sums and the valences. It has been proposed (Brown & Shannon, 1973) that second-nearest neighbours might account for some of the additional deviations. Inductive effects are also important for compounds with weak bonding, whereas it is in doubt whether the usual analytical expressions are valid for the very weak contributions.

The results allow some interesting conclusions to be made concerning Mo—N binding. Complexes with molybdenum in the 6+ oxidation state that lack terminal O atoms are the nitrido complexes, where N^{3-} is isoelectronic with O^{2-}. The Mo^{VI}—N bond length of 1·66 (4) Å in $AsPh_4[MoCl_4N]$ (Knopp, Lörcher & Strähle, 1977) and the Mo^{VI}—N—Mo^{VI} distances of 1·64–1·67 (1) Å and 2·14–2·20 (1) Å in $[MoCl_3N]$ (Strähle, 1970), and of 1·659–1·661 (5) Å and 2·150–2·167 (5) Å in $[MoCl_3N(POCl_3)]_4$ (Strähle, Weiher & Dehnicke, 1978) have been described in terms of triple and single bonds. The present analysis suggests here bond strengths of about 2·5 and 0·5 v.u. Using force constants derived from vibrational spectra, Goubeau (1966) ascribes a *Bindungsgrad* of 2·2 to the multiple bond in $[MoCl_3N]$. For the short terminal monosubstituted alkyl imido moiety with a Mo^{V}—N bond length of 1·733 (4) Å in $[Mo_2(\eta^5\text{-}C_5H_5)_2\{(CH_3)_3CN\}_2(\mu\text{-}S)_2]$ (Dahl, Frisch & Gust, 1974), a bond strength of about 1·6 v.u. is suggested. Other examples of Mo—N multiple bonds are found in $[Mo(i\text{-}PrO)_3(NO)]_2$ (Chisholm, Cotton, Extine & Kelly, 1978) and amongst the mixed (N,S) ligand sets, namely in $[Mo(EtPhN_2)\{(CH_2)_5NCS_2\}_3]BPh_4$ (March, Mason & Thomas, 1975), in $[Mo(Et_2NCS_2)_3N]$, $[Mo(Me_2NCS_2)_3NS]$ and $[\{Mo(Et_2NCS_2)_3N\}_2.Mo(Et_2NCS_2)_3](PF_6)_3$ (Bishop, Chatt, Dilworth, Hursthouse & Motevalli, 1976), in $[Mo(n\text{-}Bu_2NCS_2)_3(NO)]$ (Brennan & Bernal, 1973) and in $[Mo(NC_6H_4\text{-}pCH_3)(PhCONNC_6H_4\text{-}pCH_3)(Me_2PhP)Cl_2]$ (Hursthouse & Quick, 1978), with Mo—N bond distances of 1·62–1·74 Å. For the complex $[Mo_2(\text{L-histidine})_2O_2S_2].1\frac{1}{2}H_2O$, thought to possess formal Mo—N single bonds of 2·237–2·272 (9) Å (Spivack & Dori, 1975), the present analysis suggests bond strengths of less than 0·5 v.u.

In oxo species, bridges of the type Mo(μ-O)Mo and Mo(μ-O)$_2$Mo are quite common. Mo—O bond distances in linear Mo^{V}—O—Mo^{V} bridges are 1·859 Å (Bart & Ragaini, 1979). The corresponding linear μ-N bridge has not been described, but unsymmetrical linear MoNMo moieties are found in the aforementioned nitrido complexes and in the mixed-valent complex $[\{Mo(Et_2NCS_2)_3N\}_2.Mo(Et_2NCS_2)_3](PF_6)_3$ (Bishop *et al.*, 1976), with average Mo—N distances of 1·639 and 2·143 Å in the last case. The mean Mo^{V}—O bond length in the MoO_2Mo binuclear units of Table 1 is 1·938 Å, corresponding to 0·84 v.u.; the corresponding average Mo^{V}—Mo^{V} distance is 2·563 Å. An asymmetrical diazenido bridge Mo^{V}—Mo^{V} distance of 2·662 Å and an average Mo^{V}—N bond length of 1·938 Å have been found in $[Mo_2(PhCON_2)_2(Et_2NCS_2)_2O]$ (Bishop, Chatt, Dilworth, Kaufman, Kim & Zubieta, 1977). Although this bridge is not strictly comparable to the aforementioned di-μ-oxo bridges due to differences in the ligancy of the bridging atom, the calculated Mo—N bond strength is similar (0·89 v.u.). Finally, while an Mo(μ-O)$_3$Mo bridge has been reported in [Mo$_2$(pq)$_2$O$_5$].CH$_2$Cl$_2$ (pq = 9,10-phenanthrenequinone) (Pierpont & Buchanan, 1975) with an Mo^{VI}–Mo^{VI} distance of 3·160 (2) Å, corresponding binuclear nitrido complexes are unknown.

All calculations were performed on the Oxford University ICL 1906A computer.

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